JC02 Rec'd PCT/PTO 27 MAR 2002

FORM PTO-1390
(REV. 12-2001)

U S DEPARTMENT OF [illegible]RCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

AT[illegible]NEY'S DOCKET NUMBER
Mo-7059/LeA 33,071

U S. APPLICATION NO (If known, see 37 CFR 1 5
~~To Be Assigned~~ 10/089358

INTERNATIONAL APPLICATION NO. PCT/EP00/09269	INTERNATIONAL FILING DATE 18 September 2000 (18.09.00)	PRIORITY DATE CLAIMED 01 October 1999 (1.10.99)

TITLE OF INVENTION
METHOD FOR DIGITALLY AND OPTICALLY STORING DATA

APPLICANT(S) FOR DO/EO/US BERNETH, Horst; BIERINGER, Thomas; EICKMANS, Johannes; JACOBSEN, Wolfgang and KOSTROMINE, Serguei

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is attached hereto (required only if not communicated by the International Bureau).
   b. ☐ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English lanugage translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract

JC13 Rec'd PCT/PTO 27 MAR 2002

U.S. APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
To Be Assigned 10/089358	PCT/EP00/09269	Mo-7059/LeA 33,071

21. ☒ The following fees are submitted:

	CALCULATIONS	PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 0.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total claims	27 - 20 =	7	x **$18.00**	$ 126.00	
Independent claims	2 - 3 =	0	x **$84.00**	$ 0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$ 0.00	

TOTAL OF ABOVE CALCULATIONS =	$ 1,016.00	
☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. +	$ 0.00	
SUBTOTAL =	$ 1,016.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).	$ 0.00	
TOTAL NATIONAL FEE =	$ 1,016.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +	$ 0.00	
TOTAL FEES ENCLOSED =	$ 1,016.00	
	Amount to be refunded:	$
	charged:	$

a. ☐ A check in the amount of $ ________________ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of $ 1,016.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848 A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

00157
PATENT TRADEMARK OFFICE

SIGNATURE

Aron Preis
NAME

29,426
REGISTRATION NUMBER

10/089358
JC13 Rec'd PCT/PTO 27 MAR 2002

PATENT APPLICATION
Mo-7059
LeA 33,071

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
) PCT/EP00/09269
HORST BERNETH ET AL)
)
SERIAL NUMBER: TO BE ASSIGNED)
)
FILED: HEREWITH)
)
TITLE: METHOD FOR DIGITALLY AND)
OPTICALLY STORING DATA)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231
Sir:

Prior to the examination of the instant patent application kindly amend the enclosed translation thereof as follows:

"Express Mail" mailing label number ET671453181US
Date of Deposit March 27, 2002

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch
(Name of person mailing paper or fee)

Signature of person mailing paper or fee)

IN THE SPECIFICATION:

In page 1, please replace the title with the following:

-- METHOD FOR DIGITALLY AND OPTICALLY STORING DATA --

Please add an abstract page reading as follows:

-- METHOD FOR DIGITALLY AND OPTICALLY STORING DATA

ABSTRACT OF THE DISCLOSURE

A process for the optical writing of optically readable digital information in a two dimensional extended storage medium is disclosed. The process is characterized in that on account of the optical writing process the surface topography of the storage medium is suitable and sufficiently modified for the optical reading process. --

IN THE CLAIMS:

Cancel Claims 25 and 26.

Please amend the claims as follows:

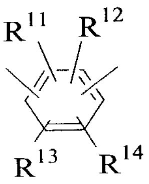
4. Process according to Claim 1, in which a storage medium is used and the light-active layer predominantly comprises oligomers and/or polymers containing dyes that orientate under the action of light, preferably amorphous polymers, particularly preferably side group polymers.

5. Process according to Claim 1, characterised in that a polymer film whose mass density is closely matched to that of the light-active layer is used as covering layer.

6. Process according to Claim 1, wherein as light-active polymer films side-chain polymers, optionally block polymers and/or graft polymers are used, to which dyes are bound as side chains via a STQ-spacer (formula I) and dimensionally anisotropic groups are likewise bound via a STQ-spacer (formula II), wherein formula I has the structure

$$-S^1-T^1-Q^1-X^{1'}-Ar^1-\left(X^{2'}-Ar^2\right)_y\left(X^{3'}-Ar^3\right)_z-X^4 \qquad (I)$$

where -Ar^1- =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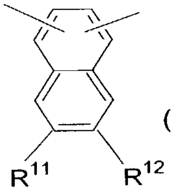
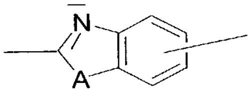
(III)

or



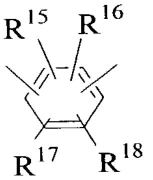
(IV)

or



(V)

where -Ar^2- =


R15
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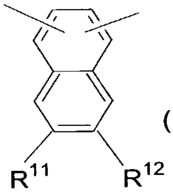
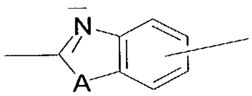
(VI)

or



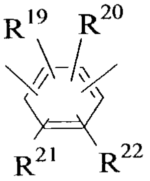
(IV)

or



(V)

where -Ar^3- =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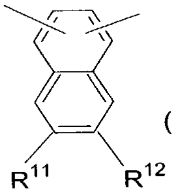
R20
R21
R22

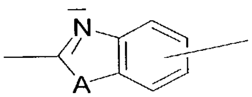
(VII)

or



(IV)

or



(V)

in which

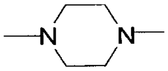
y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings, if y and/or z denote 2,

A denotes O, S or N-C_1- to C_4-alkyl,

Q^1 and Q^2 independently of one another denote -O-, -S-, -(N-R^5)-, -C(R^6R^7)$_p$, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -(C=NR^8)-, -(CNR^8-NR^5)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote -(CH_2)$_p$-, wherein the chain may be interrupted by -O-, -NR^9-, or -OSi$R^{10}{}_2$O- and may be substituted by methyl,

S^1 and S^2 independently of one another denote a direct bond, -O-, -S- or -NR^9-,

P denotes an integer from 2 to 12, preferably 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl, ethyl, or propyl ,

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen or a non-ionic substituent,

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, -COO-C_1- to C_4-alkyl or $X^{4'}$-R^4,

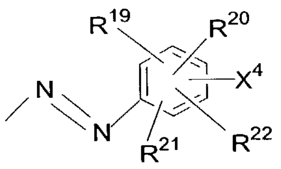
$X^{1'}$, $X^{2'}$ $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -S-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-, -(CO-O)-, -(CO-NR^5)-, -(SO_2)-, -(SO_2-O)-, (SO_2-NR^5)-, or -(CNR^8-NR^5)- and

$X^{2'}$ and $X^{3'}$ may in addition denote -(C=NR^8)-, -(N=N)- and at least one of the groups $X^{2'}$or $X^{3'}$ denotes -N=N-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-, C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O), C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2), C_2- to C_{20}-alkenyl-(SO_2)- or C_6- to C_{10}-aryl-(SO_2), wherein

by the term non-ionic substituents are understood halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_1- C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O)-, C_1- to C_{20}-alkyl-NH-(C=O)-, C_6 to C_{10}-aryl-NH-(C=O)- or a radical of the formula



(VIII)

and the alkyl, cycloalkyl, alkenyl and aryl radicals in turn may be substituted by up to 3 radicals from the group comprising halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl or C_6- to C_{10}-aryl, and the alkyl and alkenyl radicals may be straight-chain or branched, and

by the term halogen is understood fluorine, chlorine, bromine and iodine, in particular fluorine and chlorine,

and formula II is described by

$$-S^1-T^1-Q^1-X^{1'}-Ar^1-\left(X^{2'}-Ar^2\right)_y-\left(X^{3'}-Ar^3\right)_z-X^4 \qquad (II)$$

wherein the above substituent definitions (formula I) are also valid for formula II, with the proviso that none of the groups $X^{2'}$ or $X^{3'}$ may denote -N=N- and R^{11} to R^{22} may not denote a radical of the formula (VIII).

8. Process according to Claim 1, wherein the storage medium on which information is to be written has a light-active layer of a thickness between 0.05 and 1000 µm.

9. Process according to Claim 1, wherein the storage medium that is used has an optical density at the wavelength of the writing laser of the light-active layer of between 0.3 and 20.

10. Process according to Claim 1, wherein in the storage medium that is used a depression is produced as a change in the surface topography of the light-active layer, said depression preferably having a depth of at least 10 nm.

11. Process according to Claim 1, characterised in that a depression is produced in the storage medium having a width in one direction, measured on the original surface, of at least 10 µm.

12. Process according to Claims 1, characterised in that the change in the surface topography of the storage medium is produced by laser light, preferably having wavelengths between 380 nm and 820 nm.

13. Process according to Claim 1, characterised in that the light has an intensity of between 150 μW and 100 mW and is focused on spots having a dimension (full half-value width) in a range between 10 nm and 8 μm.

14. Process according to Claim 1, characterised in that information can be written on storage media whose carrier layer comprises a polymer, preferably a thermoplastic polymer, particularly preferably polycarbonate.

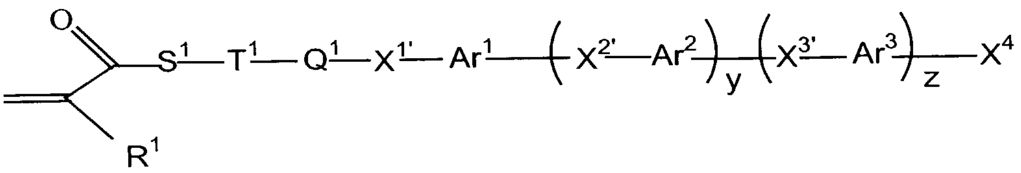
15. Process according to Claim 1, characterised in that a signal deviation is written in the storage medium having at least a carrier/noise ratio of 20 dB.

16. Process according to Claim 1, wherein information can be written on storage media that contain, between the dye-containing layer and the further layer, an additional, light-reflecting layer, preferably from the group of metals comprising aluminium, silver, gold, particularly preferably from the group comprising aluminium and silver, and most particularly preferably aluminium.

17. Process according to Claim 1, wherein the storage medium on which information is to be written has no reflecting layer.

18. Process according to Claim 1, characterised in that the optical writing process is performed with polarised light of variable intensity, produced by a LASER with an acousto-optical modulator or by modulation of a LASER diode, and the polarisation state of the reflected light is detected in a polarisation optics system.

19. Monomers of the formula

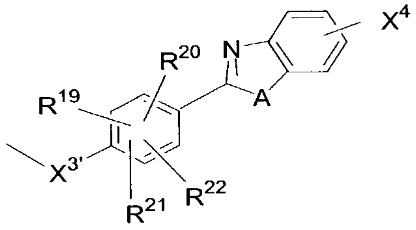


(Ia)

wherein R^1 denotes hydrogen or methyl and

the other radicals have the meanings defined in Claim 6, and

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula

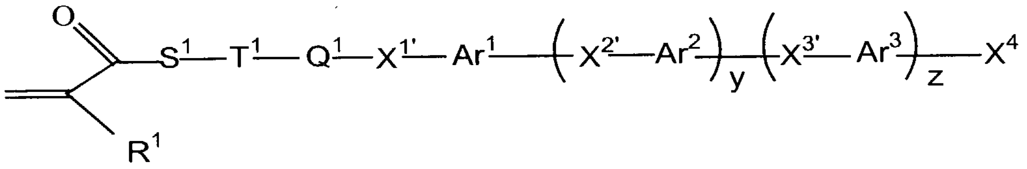

X4
R20
N
A
R19
X3'
R21
R22

$X^{3'}$ denotes –N=N- or –CO-NH-.

24. Polymers produced from monomers according to Claim 19.

The following new claims have been added:

--27. Monomers of the formula

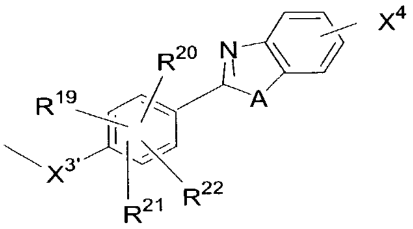

O
S1
T1
Q1
X1'
Ar1
X2'
Ar2
y
X3'
Ar3
z
X4
R1

(Ia)

wherein R^1 denotes hydrogen or methyl and

the other radicals have the meanings defined in Claim 7, and

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula



X4
R20
N
A
R19
X3'
R21
R22

$X^{3'}$ denotes –N=N- or –CO-NH-.

28. A method of using the monomers of Claim 19 comprising producing an optical storage medium.

29. The storage medium prepared by the method of Claim 18.--

REMARKS

The present amendment seeks to place the application in better conformance with U.S. practice. A page containing an Abstract of the Disclosure is enclosed.

Entry of the amendment is requested.

Respectfully submitted,

By ______________________
Aron Preis
Attorney for Applicants
Reg. No. 29,426

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100 Bayer Road
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(412) 777-8343
FACSIMILE PHONE NUMBER:
(412) 777-8363

s:/sr/ap0285

VERSION WITH MARKINGS TO SHOW CHANGES MADE:

IN THE SPECIFICATION:

In page 1, the title has been replaced with the following:

-- METHOD FOR DIGITALLY AND OPTICALLY STORING DATA --.

The following Abstract of the Disclosure has been added:

-- METHOD FOR DIGITALLY AND OPTICALLY STORING DATA

ABSTRACT OF THE DISCLOSURE

A process for the optical writing of optically readable digital information in a two dimensional extended storage medium is disclosed. The process is characterized in that on account of the optical writing process the surface topography of the storage medium is suitable and sufficiently modified for the optical reading process. --

IN THE CLAIMS:

Claims 25 and 26 have been deleted.

The following claims have been amended as follows:

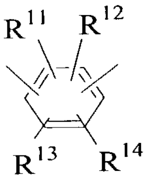
4. Process according to [one or more of the preceding claims] Claim 1, in which a storage medium is used and the light-active layer predominantly comprises oligomers and/or polymers containing dyes that orientate under the action of light, preferably amorphous polymers, particularly preferably side group polymers.

5. Process according to [one or more of the preceding claims] Claim 1, characterised in that a polymer film whose mass density is closely matched to that of the light-active layer is used as covering layer.

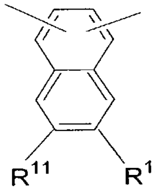
6. Process according to [one or more of the preceding claims] Claim 1, wherein as light-active polymer films side-chain polymers, optionally block polymers and/or graft polymers are used, to which dyes are bound as side chains via a STQ-spacer (formula I) and dimensionally anisotropic groups are likewise bound via a STQ-spacer (formula II), wherein formula I has the structure

$$-S^1-T^1-Q^1-X^{1'}-Ar^1-\left(X^{2'}-Ar^2\right)_y-\left(X^{3'}-Ar^3\right)_z-X^4 \qquad \text{(I)}$$

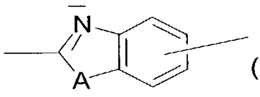
where -Ar^1- =


R11
R12
R13
R14

(III) or

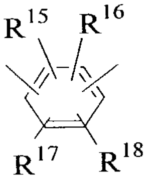


(IV) or



(V)

where -Ar^2- =


R15
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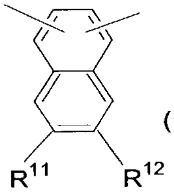
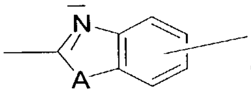
R17
R18

(VI) or

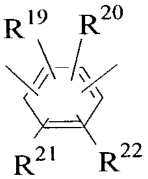


(IV) or

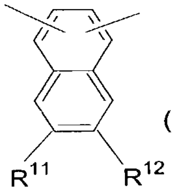


(V)

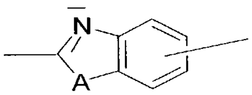
where -Ar^3- =


R19
R20
R21
R22

(VII) or



(IV) or



(V)

in which

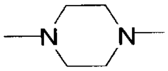
y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings, if y and/or z denote 2,

A denotes O, S or N-C_1- to C_4-alkyl,

Q^1 and Q^2 independently of one another denote -O-, -S-, -(N-R^5)-, -C(R^6R^7)$_p$, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -(C=NR^8)-, -(CNR^8-NR^5)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote -(CH_2)$_p$-, wherein the chain may be interrupted by -O-, -NR^9-, or -$OSiR^{10}{}_2O$- and may be substituted by methyl,

S^1 and S^2 independently of one another denote a direct bond, -O-, -S- or -NR^9-,

P denotes an integer from 2 to 12, preferably 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl, ethyl, or propyl ,

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen or a non-ionic substituent,

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, -COO-C_1- to C_4-alkyl or $X^{4'}$-R^4,

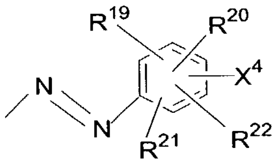
$X^{1'}$, $X^{2'}$ $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -S-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-, -(CO-O)-, -(CO-NR^5)-, -(SO_2)-, -(SO_2-O)-, (SO_2-NR^5)-, or -(CNR^8-NR^5)- and

$X^{2'}$ and $X^{3'}$ may in addition denote -(C=NR^8)-, -(N=N)- and at least one of the groups $X^{2'}$or $X^{3'}$ denotes -N=N-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-, C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O), C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2), C_2- to C_{20}-alkenyl-(SO_2)- or C_6- to C_{10}-aryl-(SO_2), wherein

by the term non-ionic substituents are understood halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_1- C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O)-, C_1- to C_{20}-alkyl-NH-(C=O)-, C_6 to C_{10}-aryl-NH-(C=O)- or a radical of the formula



(VIII)

and the alkyl, cycloalkyl, alkenyl and aryl radicals in turn may be substituted by up to 3 radicals from the group comprising halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl or C_6- to C_{10}-aryl, and the alkyl and alkenyl radicals may be straight-chain or branched, and

by the term halogen is understood fluorine, chlorine, bromine and iodine, in particular fluorine and chlorine,

and formula II is described by

$$—S^1—T^1—Q^1—X^{1'}—Ar^1—\left(X^{2'}—Ar^2\right)_y—\left(X^{3'}—Ar^3\right)_z—X^4 \qquad \text{(II)}$$

wherein the above substituent definitions (formula I) are also valid for formula II, with the proviso that none of the groups $X^{2'}$ or $X^{3'}$ may denote -N=N- and R^{11} to R^{22} may not denote a radical of the formula (VIII).

8. Process according to [one or more of the preceding claims] Claim 1, wherein the storage medium on which information is to be written has a light-active layer of a thickness between 0.05 and 1000 µm.

9. Process according to [one or more of the preceding claims] Claim 1, wherein the storage medium that is used has an optical density at the wavelength of the writing laser of the light-active layer of between 0.3 and 20.

10. Process according to [one or more of the preceding claims] Claim 1, wherein in the storage medium that is used a depression is produced as a change in the surface topography of the light-active layer, said depression preferably having a depth of at least 10 nm.

11. Process according to [one or more of the preceding claims] Claim 1, characterised in that a depression is produced in the storage medium having a width in one direction, measured on the original surface, of at least 10 µm.

12. Process according to [one or more of the preceding claims] Claims 1, characterised in that the change in the surface topography of the storage medium is produced by laser light, preferably having wavelengths between 380 nm and 820 nm.

13. Process according to [one or more of the preceding claims] Claim 1, characterised in that the light has an intensity of between 150 µW and 100 mW and is focused on spots having a dimension (full half-value width) in a range between 10 nm and 8 µm.

14. Process according to [one or more of the preceding claims] Claim 1, characterised in that information can be written on storage media whose carrier layer comprises a polymer, preferably a thermoplastic polymer, particularly preferably polycarbonate.

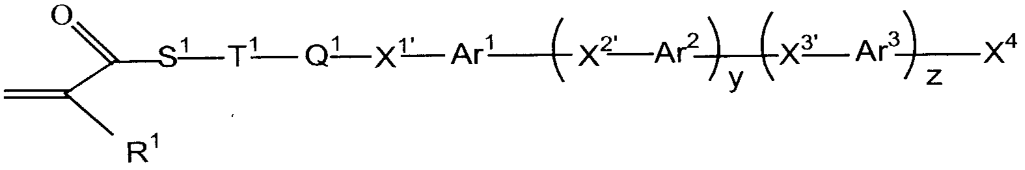
15. Process according to [one or more of the preceding claims] Claim 1, characterised in that a signal deviation is written in the storage medium having at least a carrier/noise ratio of 20 dB.

16. Process according to [one or more of the preceding claims] Claim 1, wherein information can be written on storage media that contain, between the dye-containing layer and the further layer, an additional, light-reflecting layer, preferably from the group of metals comprising aluminium, silver, gold, particularly preferably from the group comprising aluminium and silver, and most particularly preferably aluminium.

17. Process according to [one or more of the preceding claims] Claim 1, wherein the storage medium on which information is to be written has no reflecting layer.

18. Process according to [one or more of the preceding claims] Claim 1, characterised in that the optical writing process is performed with polarised light of variable intensity, produced by a LASER with an acousto-optical modulator or by modulation of a LASER diode, and the polarisation state of the reflected light is detected in a polarisation optics system.

19. Monomers of the formula

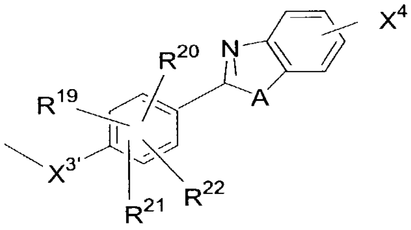


$$CH_2=C(R^1)-CO-S^1-T^1-Q^1-X^{1'}-Ar^1-(X^{2'}-Ar^2)_y-(X^{3'}-Ar^3)_z-X^4$$ (Ia)

wherein R^1 denotes hydrogen or methyl and

the other radicals have the meanings defined in [claims 6 and 7] Claim 6, and

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula

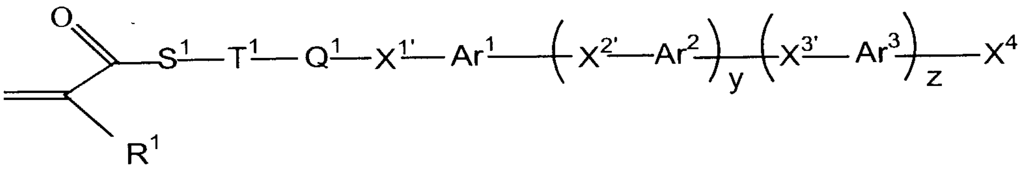


$X^{3'}$ denotes –N=N- or –CO-NH-.

24. Polymers produced from monomers according to [one or more of the preceding claims] Claim 19.

The following new claims have been added:

--27. Monomers of the formula

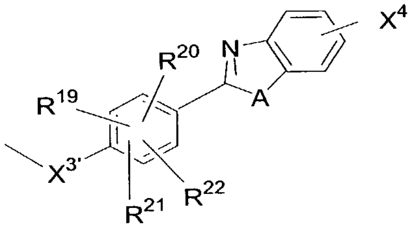


$$CH_2=C(R^1)-CO-S^1-T^1-Q^1-X^{1'}-Ar^1-(X^{2'}-Ar^2)_y-(X^{3'}-Ar^3)_z-X^4$$ (Ia)

wherein R^1 denotes hydrogen or methyl and

the other radicals have the meanings defined in Claim 7, and

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula



$X^{3'}$ denotes –N=N- or –CO-NH-.

28. A method of using the monomers of Claim 19 comprising producing an optical storage medium.

29. The storage medium prepared by the method of Claim 18.--

METHOD FOR DIGITALLY AND OPTICALLY STORING DATA

ABSTRACT OF THE DISCLOSURE

A process for the optical writing of optically readable digital information in a two dimensional extended storage medium is disclosed. The process is characterized in that on account of the optical writing process the surface topography of the storage medium is suitable and sufficiently modified for the optical reading process.

WO 01/26105

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Donna J. Veatch
(Name of person mailing paper or fee)
Signature of person mailing paper or fee)

10/089358

JC13 Rec'd PCT/PTO 27 MAR 2002

Process for the Digital Optical Storage of Data

The present invention relates to a process for the optical writing and also subsequent optical reading of digital information in a two-dimensional extended storage medium.

It is already known and is commercially intensively utilised to store digital data in the form of local changes in the surface topography, so-called pits, on plastics disks, in order subsequently to read the digital data using an optical measurement system (EP-A 25253). This concept forms the basis of the present-day market-dominating technique for reproducing audio recordings (audio-CD) and computer software (CD-ROM). It is however not possible to write information optically. Instead, in a costly and complicated multi-stage process a mould is produced that transfers the data information in an injection moulding stamping process onto each individual CD. Accordingly this technique is economically viable only in mass production.

It is also possible to store digital data in the form of local differences in absorption capacity for visible light in plastics disks in such a way that the digital data can be read again using an optical measurement system. This measurement system is extremely similar to or indeed identical to the measurement system for reading the injection moulding stamped audio-CDs or CD-ROMs mentioned above. In this case the plastics disk contains a coating having a dye whose absorption behaviour can be so strongly changed by light of a suitable wavelength that this change can subsequently be scanned using light of a generally lesser intensity without thereby also affecting the absorption behaviour of the hitherto unchanged regions (Y.J. Huh et al. Jpn. J. Appl. Phys. Vol 36 (1997), p. 7233 - 7238). A commonly available CD-R is built up from several layers. Tracking grooves (pregrooves) are stamped in the supporting material consisting of, *inter alia*, polycarbonate, on which supporting material is arranged a thin dye layer followed by a reflecting layer consisting of, *inter alia*, gold, which is protected by a coating lacquer.

In principle various light-induced processes are responsible for the changed absorption behaviour of the CD-R: the writing laser is focused through the substrate onto the dye. The light-absorbing dye serves primarily as an absorption source for the incident light quanta and is optimised as regards its absorption behaviour to the laser sources that are used. The dye heats up due to the absorption, melts, and thereby modifies its surroundings: bubbles and other deformations that are detected by the reading laser as pit-like structures are formed in the interfaces between the dye and the polycarbonate substrate and between the dye and the gold.

Contributions from the change in the dye are also involved in the actual signal. The optical parameters of the dye are altered by, *inter alia*, its destruction, which in turn affects the read signal. At the present time three types of recording layers are mainly used:

- metal-stabilised cyanine dyes (green)
- phthalocyanine dyes (golden-brown)
- azo dyes (blue)

In all the aforementioned cases the dye simply serves as a heat source, and the pit-like deformation is not produced in the dye system itself but primarily through a modification of the adjacent boundary layers resulting from the changes produced in the dye during absorption of light.

Such storage media can be written on only once but can be read as often as desired (write once read many: WORM disk), since the intensity of the laser for reading is reduced in such a way that the energy absorbed in the dye is not sufficient to induce the aforementioned deformations. CD-Rs have two major disadvantages: on the one hand the costs of the gold reflecting layer decisively determine the manufacturing costs. Gold layers are necessary in order to meet the reflection values required by the CD specifications. In addition gold layers have the necessary chemical inertness (oxidation resistance). The other disadvantage lies in the necessarily limited storage stability. The present-day commercially available systems are highly light-sensitive, and if stored in daylight can already no longer be written on after only a few hours.

The object of the invention was accordingly to provide a process that reduces or eliminates the above disadvantages.

It has now surprisingly been found that by a suitable choice of material for the two-dimensional storage medium data can be written on this storage medium in the form of local changes in the surface topography of the dye *per se* using an optical writing system and can subsequently be optically read. In this connection the processes occurring in the adjacent boundary areas do not play an essential role, and the surface topography is affected solely by modifications in the dye system. The surface modification is manifested strongly in such a way that, with a suitably optimised reading optics system, e.g. in the form of a confocal arrangement, signal relationships between the measurement at a surface-modified point and a non-modified point that are significantly superior to the signal relationships measured in conventional CD-Rs, can be achieved also without an additional reflecting layer. The new writeable media can thus be used without any additional reflecting layer.

However, as long as the high values for the absolute reflection of the CDs mentioned in the specifications (books) of conventional audio-CDs and CD-R have to be set, then an additional reflecting layer is also necessary in the storage media according to the invention.

The process according to the invention permits the writing of digital information for example on CD-R-like plastics disks with writing speeds and storage densities that are similar to CD-R, but with the advantage of an assured long-term stability since the readability of the written information can be adversely affected only by external damage to the storage disk. The written structuring in the surface topography can be changed only by heating this layer up to the vicinity of its glass transition temperature. Due to the polymer architecture the glass transition temperature is significantly greater than 100°C, preferably greater than 150°C, which means that thermal deletion can be avoided by appropriate storage of the storage disk.

A further advantage of the process according to the invention is the significantly improved signal deviation during the optical reading of the information, compared to the hitherto commercially used processes. As has already been described above, the signal deviation is so large that an additional reflecting layer can be omitted for example when using a confocal reading process.

The invention accordingly describes a storage process in which a storage medium comprising at least one substrate layer and at least one recording layer can be induced to store digital binary or non-binary information by means of a focused laser beam that can be scanned, for example in a continuous or pulsed operation mode, over the sample surface and can be focused depending on the layer arrangement in the case of multiple layers, onto the respective function layer. Alternatively the laser scanning procedure can be omitted if relative movement between the medium and laser spot can be achieved in another way, for example by rotating the medium.

The application accordingly provides a process for the optical writing of optically readable digital information in a two-dimensional extended storage medium, characterised in that by means of the optical writing process the surface topography of the storage medium is suitably and sufficiently modified for the optical reading process, and more specifically without significant proportions of the detected signal resulting from a degradation and/or a physical or chemical modification of the areas adjacent to the active absorber layer.

As storage medium any single-layer or multi-layer material is suitable that under appropriate local illumination by light alters its surface topography in the region of this illumination to such an extent that the said region can be uniquely identified by suitable optical imaging techniques, for example by means of a confocal laser scanning microscope in a remission contrast method. Multi-layer disks with a mechanically sufficiently stable substrate, a polymer film as light-active layer and a covering layer that protects the polymer film against mechanical damage during use may preferably be mentioned as suitable storage media. Writing can take place both through the covering layer as well as through the base disk. Writing through the covering layer is preferred. The layer (covering layer, base disk) through which the writing takes place must be sufficiently transparent for the wavelength of the writing light. In the wavelength range from 400 nm to 820 nm a degree of transmission of greater than 30%, preferably greater than 80%, and particularly preferably greater than 85%, should be achieved. In the wavelength range between 380 nm and 400 nm a degree of transmission greater than 30%, preferably greater than 50%, and particularly preferably greater than 75%, should be achieved.

In the case where the reflecting layer is omitted, a multi-layer storage medium may also be formed. The actual storage layers are in this case separated from one another by layers that are not light-active. If a reflecting layer is required in order to read the information, then its absorption must be chosen so that in the case of a multi-layer storage medium (storage medium with several writeable storage layers) under laser irradiation the intensity in the corresponding layers is still sufficient to produce the desired modifications.

As material for the light-active polymer film there may preferably be mentioned polymers that carry side chains of different types on a main chain acting as backbone, at least one type of which can absorb electromagnetic radiation in the wavelength range of visible light, i.e. preferably at wavelengths between $\lambda = 380$ nm and $\lambda = 820$ nm, particularly preferably at wavelengths between $\lambda = 385$ mn and $\lambda = 780$ nm, and most particularly preferably at wavelengths between $\lambda = 385$ nm and $\lambda = 660$ nm.

The recording material used in the process according to the invention is preferably a polymeric or oligomeric organic, amorphous material, particularly preferably a side-chain polymer, and likewise particularly preferably a block copolymer and/or a graft polymer.

The main chains of the side-chain polymer are derived from the following basic structures: polyacrylate, polymethacrylate, polysiloxane, polyurea, polyurethane, polyester, polyamide or cellulose. Polyacrylate and polymethacrylate are preferred.

All side-chain polymers described in the present application and the corresponding monomers are also the subject of the application.

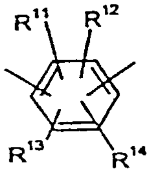
The block copolymers consist of several blocks, at least one type of which contains the copolymer systems described in more detail above. The other blocks consist of non-functionalised polymer backbones that fulfil the task of diluting the functional block in order to adjust the required optical density. The dimension of the functional block is below the visible wavelength, preferably in the region of less than 200 nm, particularly preferably less than 100 nm.

The polymerisation of the block copolymers is performed for example by free-radical or anionic polymerisation or by other suitable polymerisation processes, possibly followed by a polymer-like reaction or by a combination of these methods. The uniformity of the systems is in the region of less than 2.0, preferably less than 1.5. The molecular weight of the block copolymers obtained by free-radical polymerisation reaches values in the region of 50,000, while values of greater than 100,000 can be achieved by anionic polymerisation.

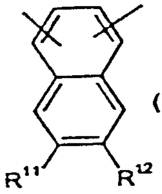
The dyes used in the process according to the invention, in particular the azo dyes, are covalently bonded as side-chains to these polymer backbones via a S-T-Q spacer

$$-S^1-T^1-Q^1-X^{1'}-Ar^1-\left(X^{2'}-Ar^2\right)_y-\left(X^{3'}-Ar^3\right)_z-X^4 \qquad (I)$$

where -Ar¹- =


R11
R12
R13
R14

(III) or



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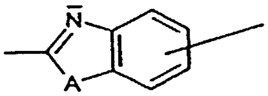
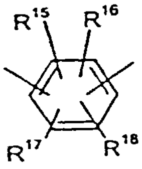
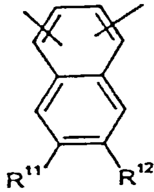


(V)

where -Ar²- =


R15
R16
R17
R18

(VI) or



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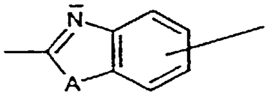

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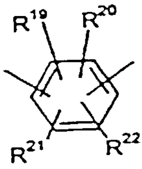
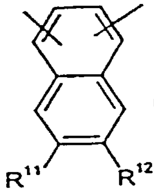
where -Ar³- =


R19
R20
R21
R22

(VII) or



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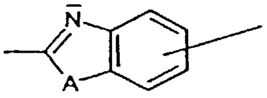


(V)

in which

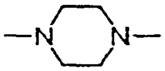
y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings, if y and/or z denote 2,

A denotes O, S or N-C_1- to C_4-alkyl,

Q^1 and Q^2 independently of one another denote -O-, -S-, -(N-R^5)-, -C(R^6R^7)$_p$, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -(C=NR^8)-, -(CNR^8-NR^5)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote -(CH_2)$_p$-, wherein the chain may be interrupted by -O-, -NR^9-, or -OSi$R^{10}{}_2$O- and may be substituted by methyl,

S^1 and S^2 independently of one another denote a direct bond, -O-, -S- or -NR^9-,

P denotes an integer from 2 to 12, preferably 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl, ethyl, propyl or C_6- to C_{10}-aryl-O-(C=O),

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen or a non-ionic substituent,

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, -COO-C_1- to C_4- alkyl or $X^{4'}$-R^4,

$X^{1'}$, $X^{2'}$, $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -S-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-,

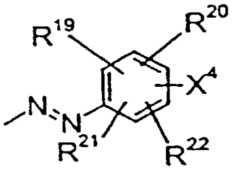
-(CO-O)-, -(CO-NR^5)-, -(SO$_2$)-, -(SO$_2$-O)-, (SO$_2$-NR^5)-, or -(CNR^8-NR^5)- and

X$^{2'}$ and X$^{3'}$ may in addition denote -(C=NR^8)-, -(N=N)- and at least one of the groups X$^{2'}$, or X$^{3'}$ denotes -N=N-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C$_1$- to C$_4$-alkyl, or C$_6$- to C$_{10}$-aryl and

R^4 and R^5 in addition independently of one another denote C$_1$- to C$_{20}$-alkyl-(C=O)-, C$_3$- to C$_{10}$-cycloalkyl-(C=O)-, C$_2$- to C$_{20}$-alkenyl-(C=O)-, C$_6$- to C$_{10}$-aryl-(C=O), C$_1$- to C$_{20}$-alkyl-(SO$_2$)-, C$_3$- to C$_{10}$-cycloalkyl-(SO$_2$), C$_2$- to C$_{20}$-alkenyl-(SO$_2$)- or C$_6$- to C$_{10}$-aryl-(SO$_2$).

Non-ionic substituents are understood to denote halogen, cyano, nitro, C$_1$- to C$_{20}$-alkyl, C$_1$- to C$_{20}$-alkoxy, phenoxy, C$_3$- to C$_{10}$-cycloalkyl, C$_2$- to C$_{20}$-alkenyl, C$_6$- to C$_{10}$-aryl, C$_1$- to C$_{20}$-alkyl-(C=O)-, C$_6$- to C$_{10}$-aryl-(C=O)-, C$_1$- to C$_{20}$-alkyl-(SO$_2$)-, C$_1$- C$_{20}$-alkyl-(C=O)-O-, C$_1$- to C$_{20}$-alkyl-(C=O)-NH-, C$_6$- to C$_{10}$-aryl-(C=O)-NH-, C$_1$- to C$_{20}$-alkyl-O-(C=O)-, C$_1$- to C$_{20}$-alkyl-NH-(C=O)-, C$_6$ to C$_{10}$-aryl-NH-(C=O)- or a radical of the formula



(VIII)

The alkyl, cycloalkyl, alkenyl and aryl radicals may in turn be substituted by up to 3 of the non-ionic substituents defined above, and the alkyl and alkenyl radicals may be straight chain or branched.

The term halogen is understood to mean fluorine, chlorine, bromine and iodine, in particular fluorine and chlorine.

The polymeric or oligomeric organic, amorphous material used in the process according to the invention may in addition to the dyes, for example of the formula (I), carry dimensionally anisotropic groupings. These two are, as a rule, bound via a spacer to the polymer backbones.

Dimensionally anisotropic groupings are described by the structure of the formula (II)

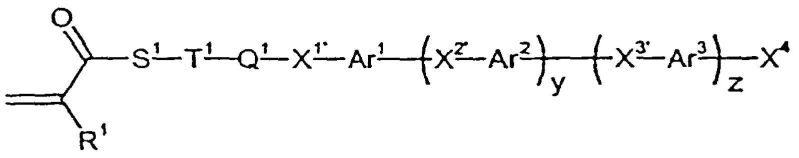
$$-S^1-T^1-Q^1-X^{1'}-Ar^1-\left(X^{2'}-Ar^2\right)_y-\left(X^{3'}-Ar^3\right)_z-X^4 \qquad \text{(II)}$$

wherein the above substituent definitions (formula I) are also valid for formula II, with the proviso that none of the groups $X^{2'}$ or $X^{3'}$ may denote -N=N- and R^{11} to R^{22} may not denote a radical of the formula (VIII).

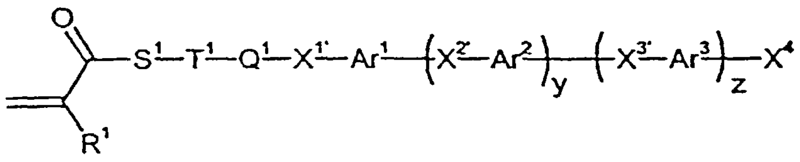
The polymers used in the process according to the invention may carry identical or different side groups of the formula (I), the radicals in the case where there are several different side groups being different, and may also carry no, identical or different side groups of the formula (II), the radicals in the case where there are several different side groups being different.

Particularly preferred are polymers that carry both side groups of the formula I and those of formula II.

Monomers with dye groups (I) and/or monomers with dimensionally anisotropic groups (II) preferably have the formulae (Ia) and (IIa):



$$CH_2=C(R^1)-C(=O)-S^1-T^1-Q^1-X^{1'}-Ar^1-\left(X^{2'}-Ar^2\right)_y-\left(X^{3'}-Ar^3\right)_z-X^4 \qquad \text{(Ia)}$$



(IIa)

wherein R^1 denotes hydrogen or methyl, and

the other radicals have the meanings given above for dye groups and dimensionally anisotropic groups.

In the process according to the invention polymers are preferably used that contain the dye side groups of the formula (I), in which

Ar^1 denotes a radical of the formula (III),

Ar^2 denotes a radical of the formula (VI),

Ar^3 denotes a radical of the formulae (VII) or (V),

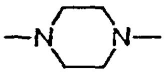
y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and $Ar^{2'}$ and/or $X^{3'}$ and Ar^3 may have different meanings if y and/or z denote 2,

A denotes O or S,

Q^1 and Q^2 independently of one another denote -O-, -(N-R^5)-, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote $-(CH_2)_p-$ wherein the chain may be interrupted by -O-, $-NR^9-$, or $-OSiR^{10}{}_2O-$ and may be substituted by methyl,

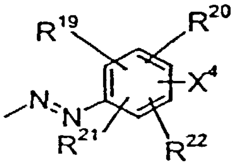
S^1 and S^2 independently of one another denote a direct bond, -O-, -S-, or $-NR^9-$

p denotes an integer from 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl or ethyl,

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen, halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alklyl-(SO_2)-, C_1- to C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O)-, C_1- to C_{20}-alkyl-NH-(C=O)-, C_6- to C_{10}-aryl-NH-(C=O)- or a radical of the formula



(VIII)

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, $-COO-C_1$ to C_4-alkyl or $X^{4'}-R^4$,

$X^{1'}$, $X^{2'}$, $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, $-(N-R^5)-$, $-C(R^6R^7)-$, -(C=O)-, -(CO-O)-, $-(CO-NR^5)-$, $-(SO_2)-$ or (SO_2-O)- and

$X^{2'}$ and $X^{3'}$ may in addition denote -(N=N)- and at least one of the groups $X^{2'}$ or $X^{3'}$ denotes -N=N-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4 alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-, C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2)-, C_2- to C_{20}-alkenyl-(SO_2)-, or C_6- to C_{10}-aryl-(SO_2)-.

Also, there are preferably used in the process according to the invention polymers that contain, in addition to dye side groups of the formula (I), dimensionally anisotropic side groups of the formula (II),

in which

Ar^1 denotes a radical of the formula (III),

Ar^2 denotes a radical of the formula (VI),

Ar^3 denotes a radical of the formulae (VII) or (V),

y denotes 1 or 2,

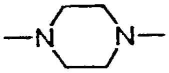
z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings if y and/or z denote 2,

A denotes O or S,

Q^1 and Q^2 independently of one another denote -O-, -(NR^5)-, -(C=O)-, -(O-CO)-,

-(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote -$(CH_2)_p$-, wherein the chain may be interrupted by -O-, -NR^9-, or -$OSiR^{10}{}_2O$- and may be substituted by methyl,

S^1 and S^2 independently of one another denote a direct bond, -O-, -S-, or -NR^9-

p denotes an integer from 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl or ethyl,

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen, halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_1- to C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O), C_1- to C_{20}-alkyl-NH-(C=O)-, or C_6- to C_{10}-aryl-NH-(C=O)-,

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, -COO-C_1 to C_4-alkyl or $X^{4'}$-R^4,

$X^{1'}$, $X^{2'}$, $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-, -(CO-O)-, -(CO-NR^5)-, -(SO_2)- or (SO_2-O)-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-, C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2)-, C_2- to C_{20}-alkenyl-(SO_2)-, or C_6- to C_{10}-aryl-(SO_2)-.

Particularly preferred are polymers according to the invention that contain the dye side groups of the formula (I),

in which

Ar^1 denotes a radical of the formula (III), wherein the two bonds are in the p-position,

Ar^2 denotes a radical of the formula (VI), wherein the two bonds are in the p- or m-position,

Ar^3 denotes a radical of the formulae (VII) or (V), wherein the two bonds in (VII) are in the p-position,

y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings if y and/or z denote 2,

A denotes O or S,

Q^1 and Q^2 independently of one another denote -O-, -(N-R^5)-, -(C=O)-, -(NR^5-CO)-, or -O-C_6H_5-COO-

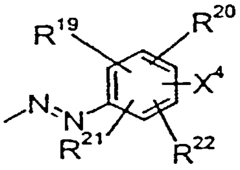
T^1 and T^2 independently of one another denote -$(CH_2)_p$-,

S^1 and S^2 independently of one another denote a direct bond, -O- or -NR^9-,

p denotes an integer from 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen or methyl,

R^{11} to R^{22} independently of one another denote hydrogen, halogen, cyano, nitro, methyl, methoxy, phenoxy, phenyl, acetyl-, benzoyl-, CH_3-(SO_2)-, CH_3-(C=O)-O-, CH_3-(C=O)-NH-, CH_3-NH-(C=O)- or a radical of the formula,



(VIII)

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3 or $X^{4'}$-R^4,

$X^{1'}$, $X^{2'}$, $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -(N-R^5)-, -(C=O)-, -(CO-NR^5)- or -(SO_2)- and

$X^{2'}$ and $X^{3'}$ may in addition denote -(N=N)- and at least one of the groups $X^{2'}$ or $X^{3'}$ denotes -N=N-,

R^4, R^5 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_4-alkyl-(C=O, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_4-alkyl-(SO_2)-, or C_6- to C_{10}-aryl-(SO_2)-.

Also, polymers are particularly preferably used in the process according to the invention that contain in addition to dye side groups of the formula (I), dimensionally anisotropic side groups of the formula (II),

in which

Ar^1 denotes a radical of the formula (III), wherein the two bonds are in the p-position,

Ar^2 denotes a radical of the formula (VI), wherein the two bonds are in the p- or m-position,

Ar^3 denotes a radical of the formulae (VII) or (V), wherein the two bonds in (VII) are in the p-position,

y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings if y and/or z denote 2,

A denotes O or S,

Q^1 and Q^2 independently of one another denote -O-, -(N-R^5)-, -(C=O)-, -(NR^5-CO)-, or -O-C_6H_5-COO-

T^1 and T^2 independently of one another denote -$(CH_2)_p$-,

S^1 and S^2 independently of one another denote a direct bond, -O- or -NR^9-,

p denotes an integer from 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen or methyl,

R^{11} to R^{22} independently of one another denote hydrogen, halogen, cyano, nitro, methyl, methoxy, phenoxy, phenyl, acetyl-, benzoyl-, CH_3-(SO_2)-, CH_3-(C=O)-O-, CH_3-(C=O)-NH-, or CH_3-NH-(C=O)-,

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3 or $X^{4'}$-R^4,

$X^{1'}$, $X^{2'}$, $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -(N-R^5)-, -(C=O)-, -(CO-NR^5)- or -(SO_2)-,

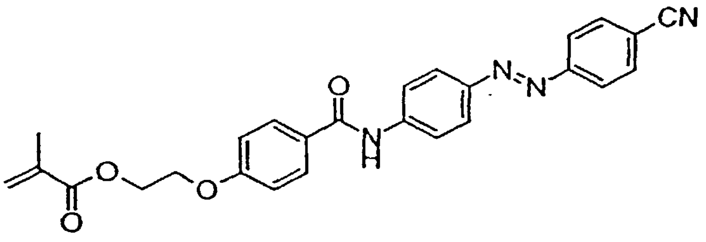
R^4, R^5 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

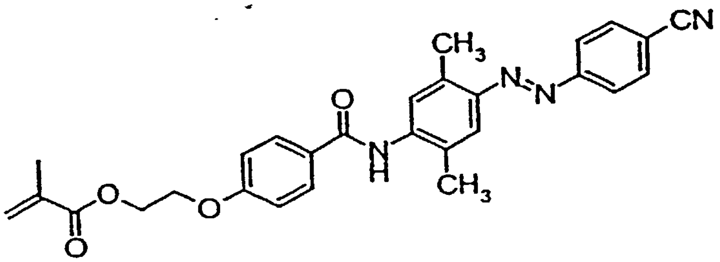
R^4 and R^5 independently of one another denote C_1- to C_4-alkyl-(C=O, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_4-alkyl-(SO_2)-, or C_6- to C_{10}-aryl-(SO_2)-.

Likewise also preferred are the monomers of the formulae (Ia) and (IIa), wherein the radicals have the preferred and particularly preferred meanings of the formulae (I) and/or (II), and

R^1 denotes hydrogen and particularly preferably denotes methyl.

Chromatophore monomers (Ia) that are particularly preferably used in the process according to the invention include:

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N
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CH3
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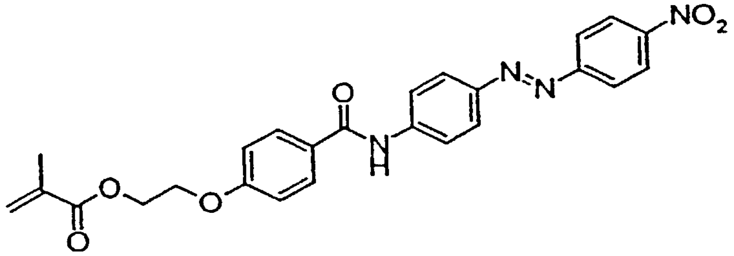
O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N=N
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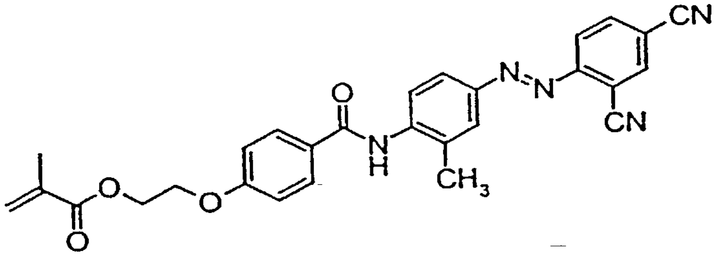
N
H
O
O
O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N=N
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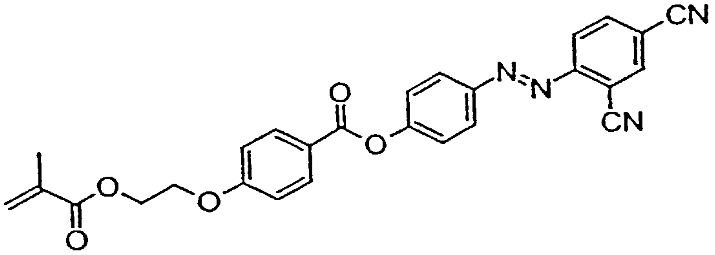
CN
N
H
CH3
O
O
O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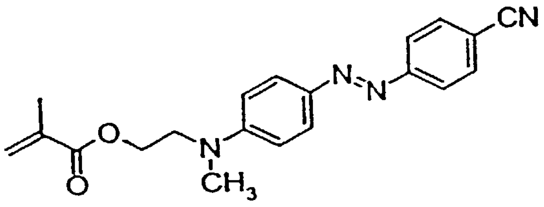
N=N
O
CN
O
O
O
O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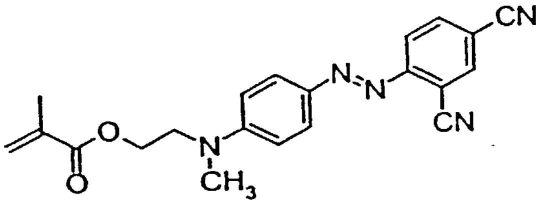
N
CH3
O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CH3
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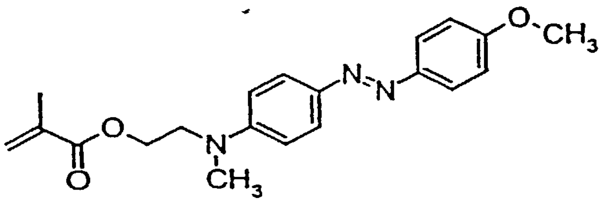
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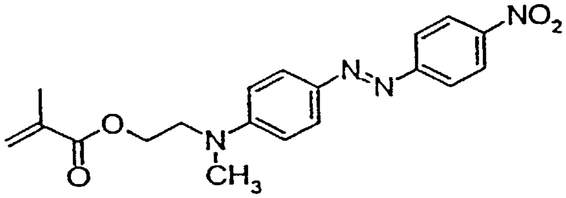
N
CH3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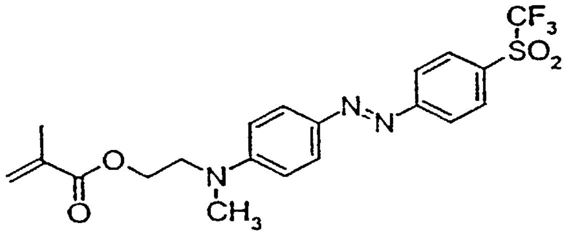
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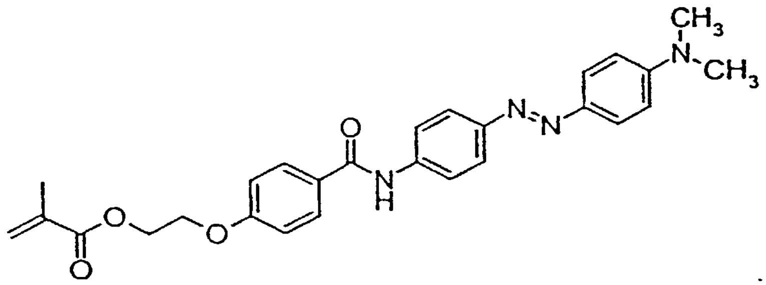
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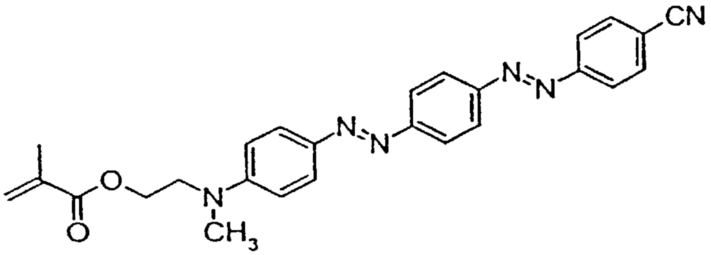
O
O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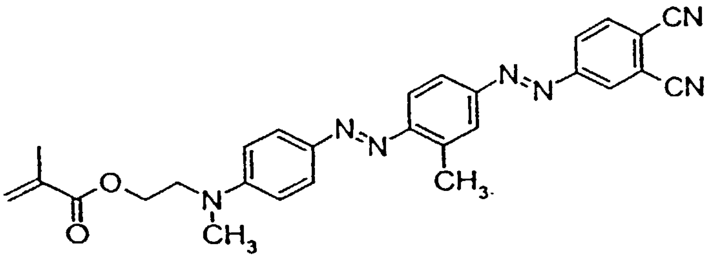
N
CH3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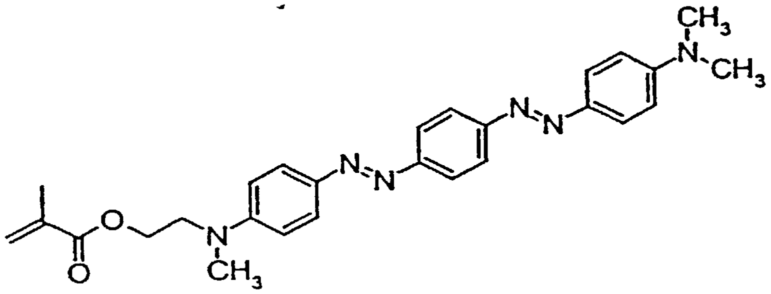
CH3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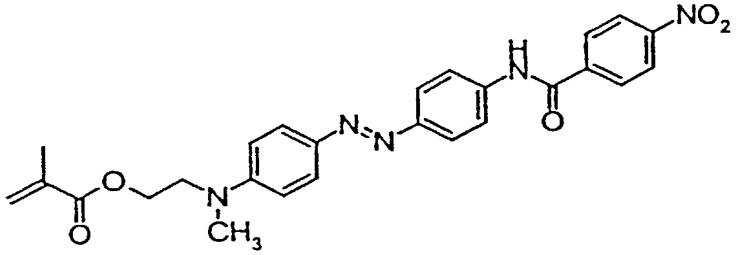
O
N
O
CH3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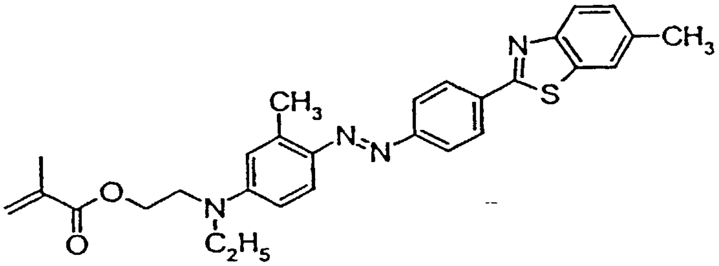
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CH3
N
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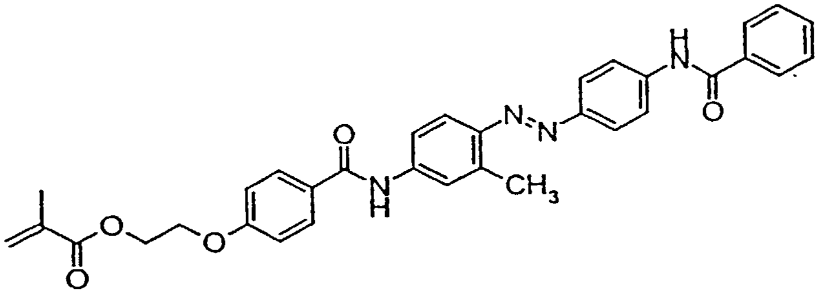
O
N
O
C2H5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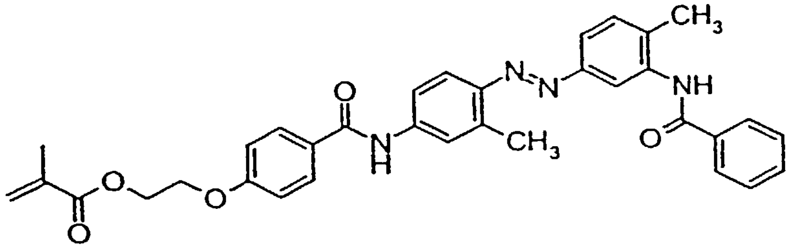
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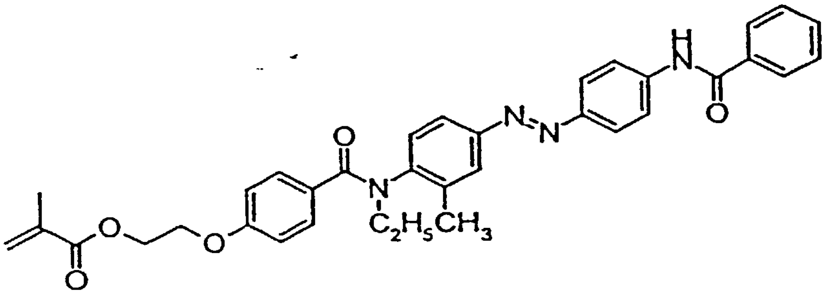
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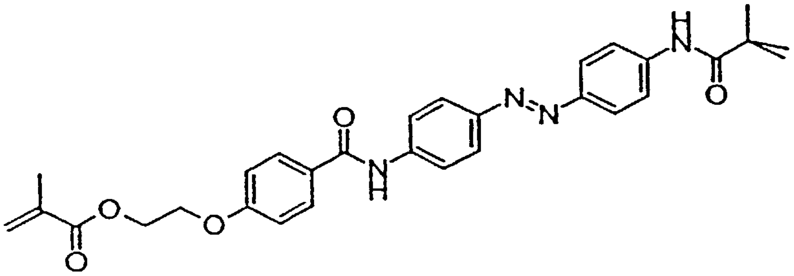
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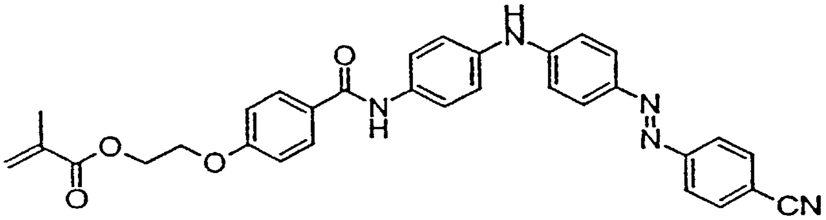
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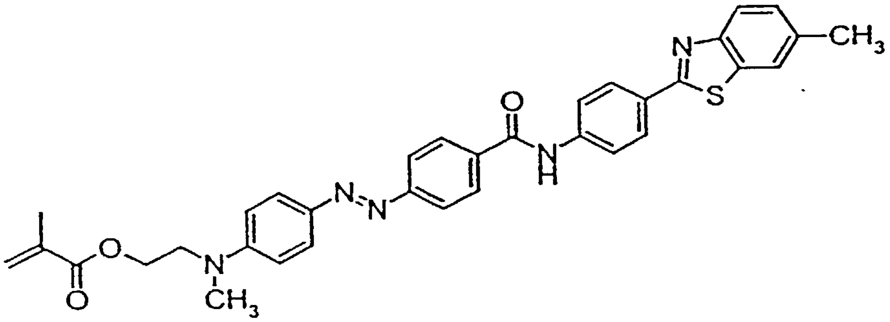
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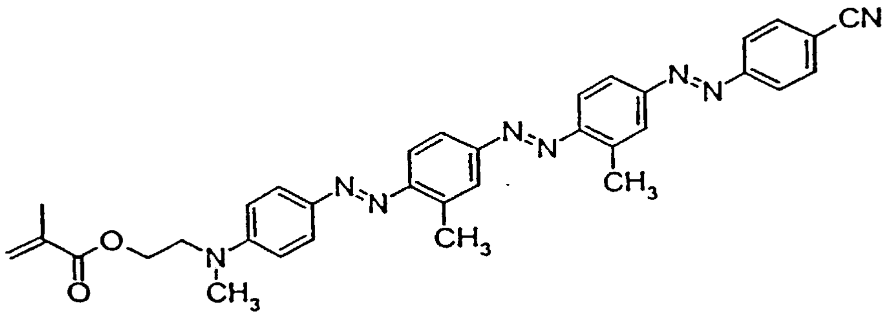
CH₃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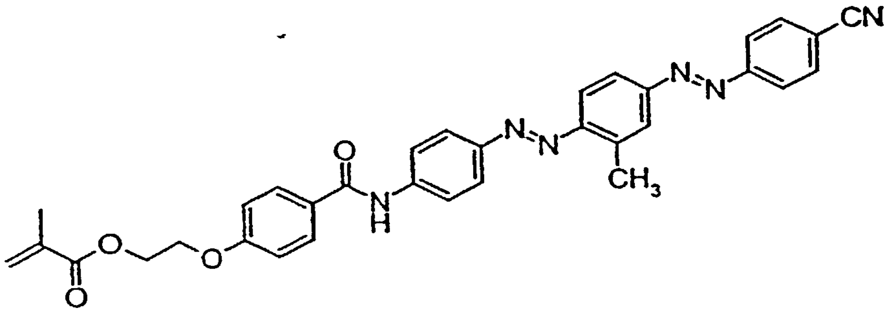
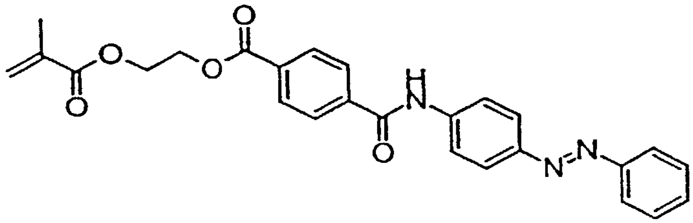
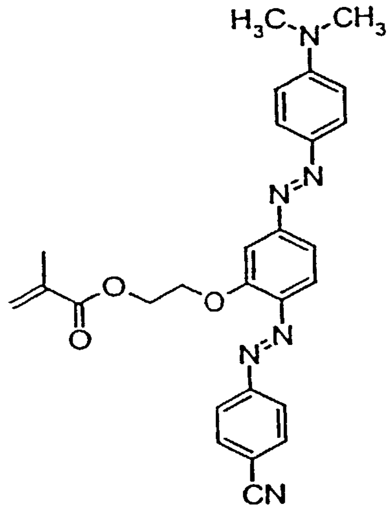
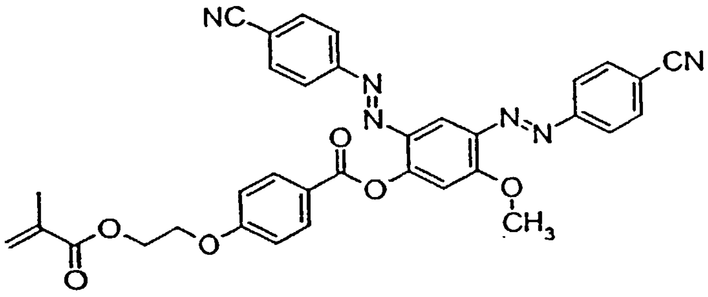
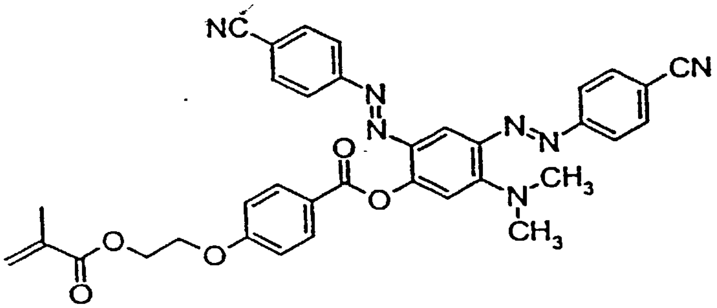
CH₃







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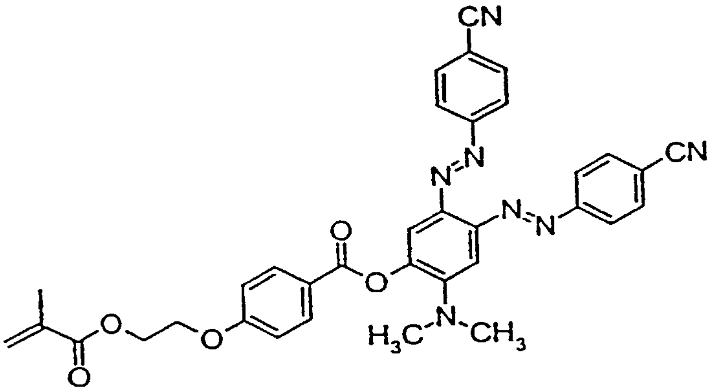
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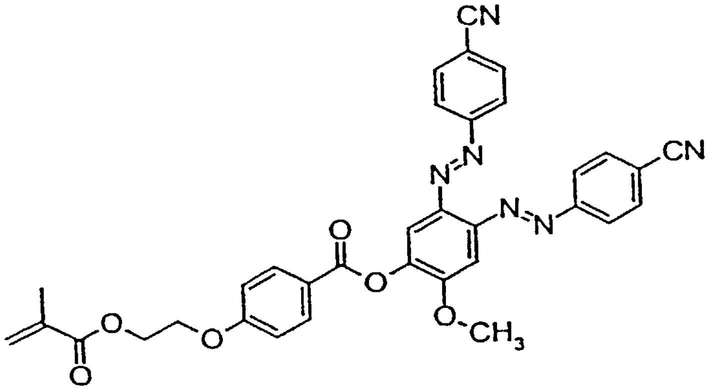
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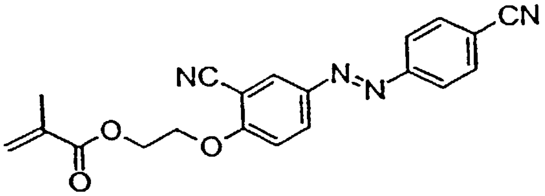
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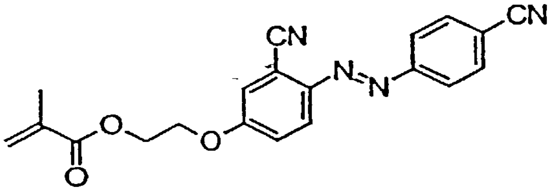
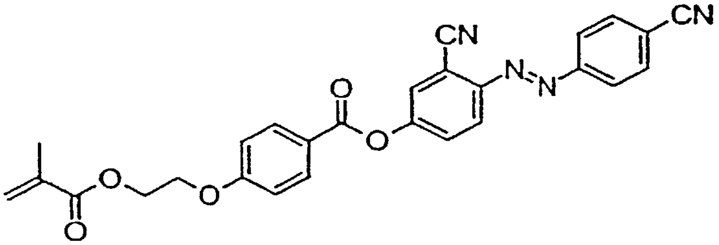
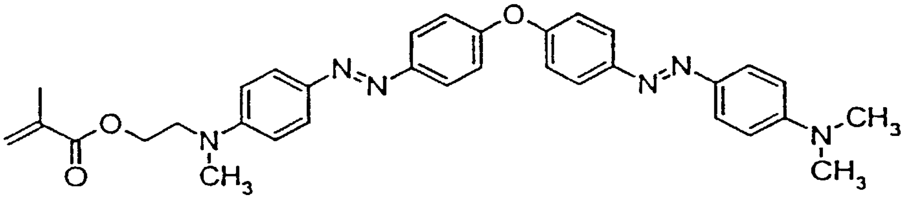
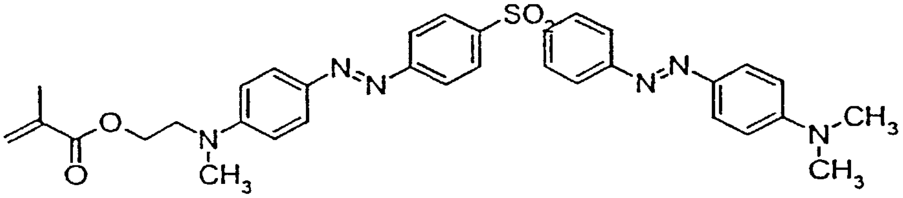
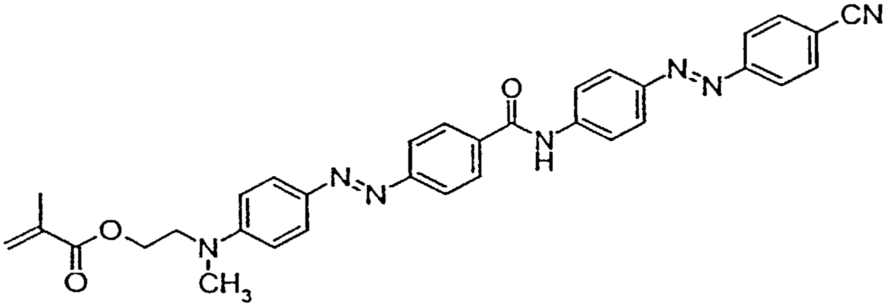
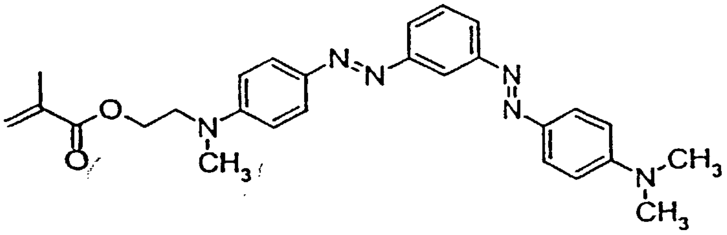


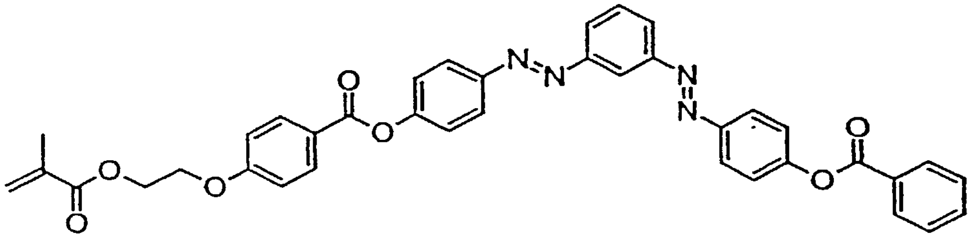


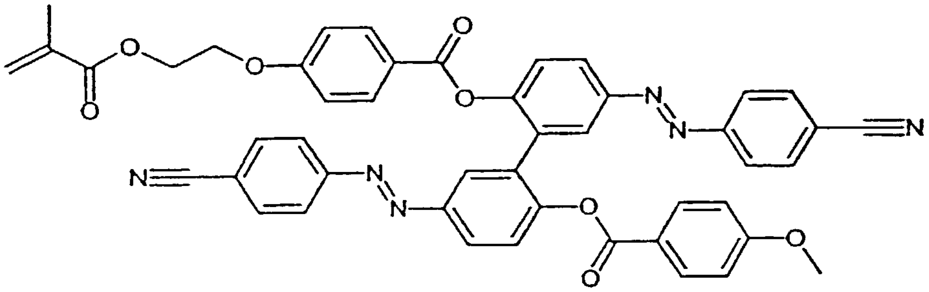


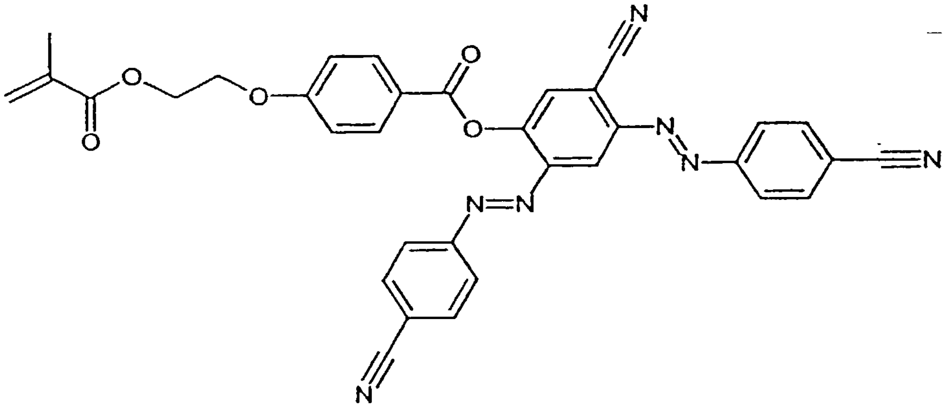


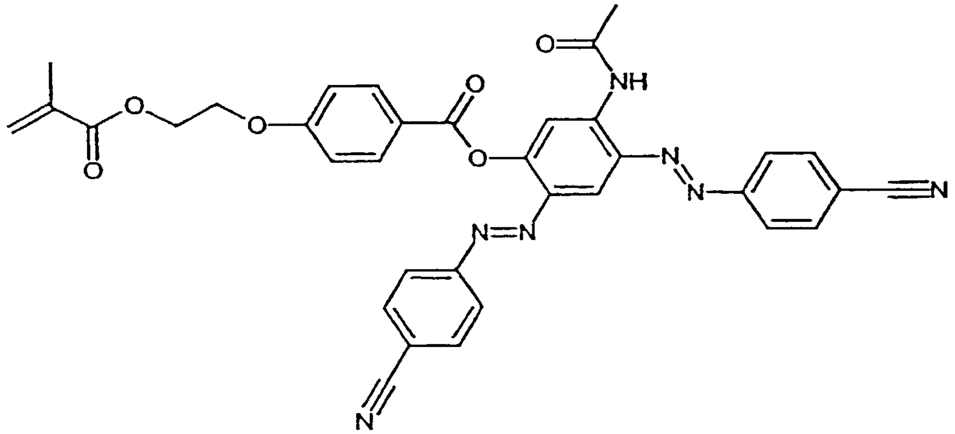


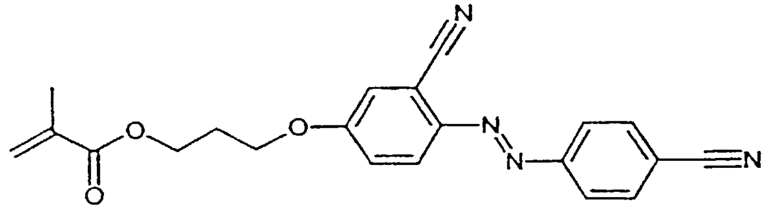


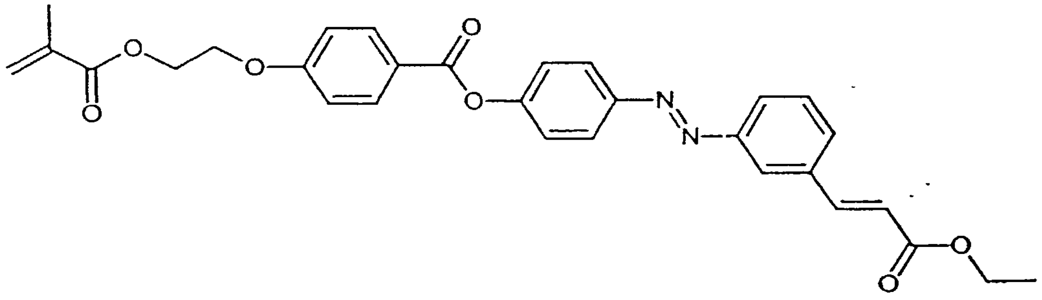


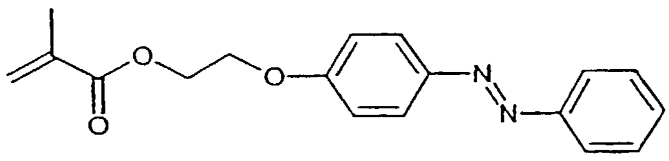




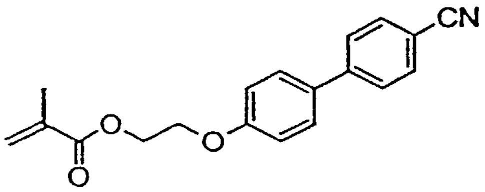


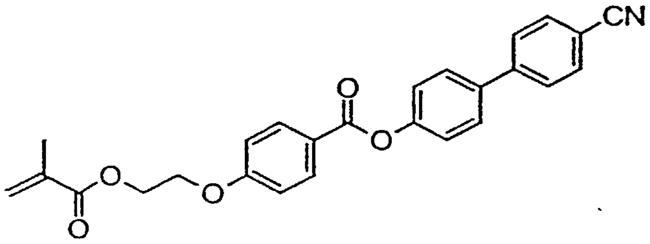


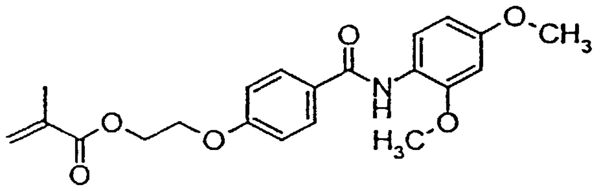




Dimensionally anisotropic monomers (IIa) that are particularly preferably used in the process include:



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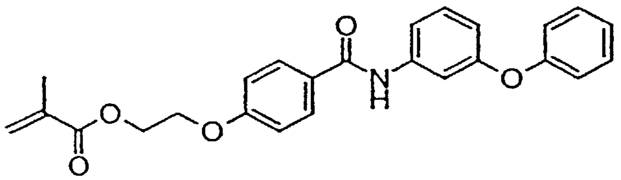
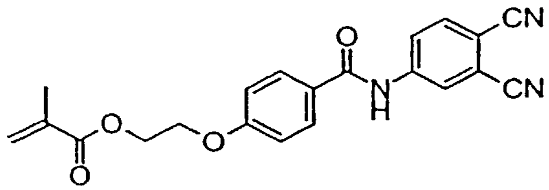
H
H3C
O
O
O
O

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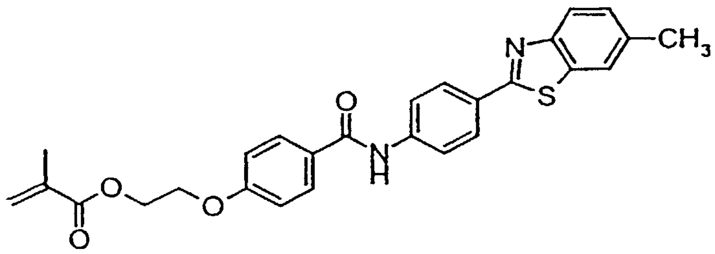
O
N
H
CN
O
O
O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S
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N
H
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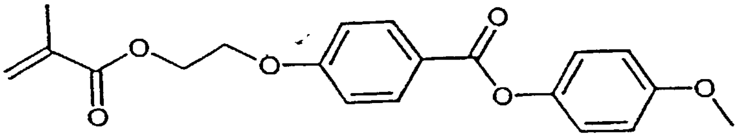
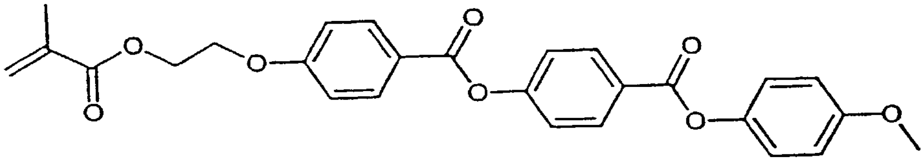
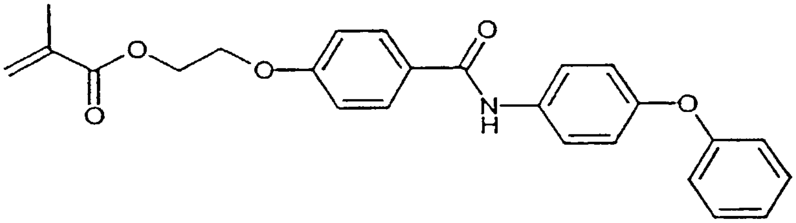
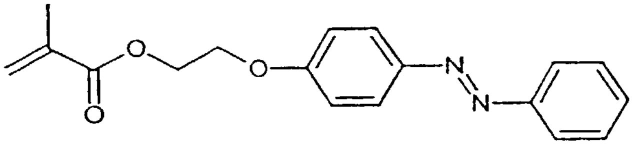
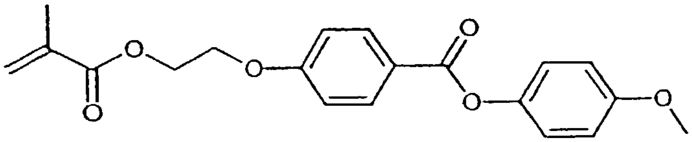






Combinations that are particularly preferably used in the process include:





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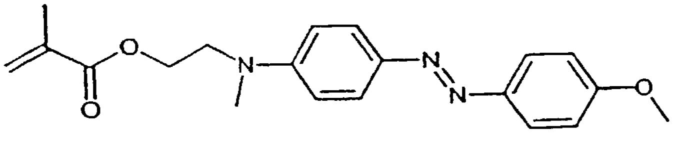

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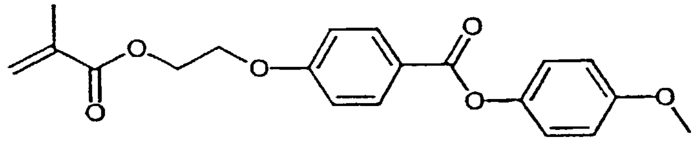

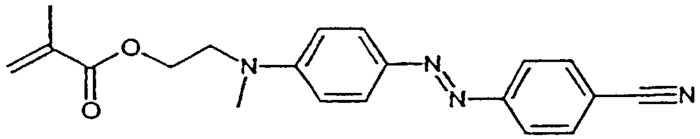

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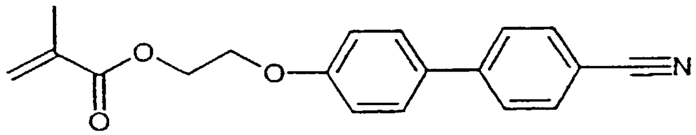

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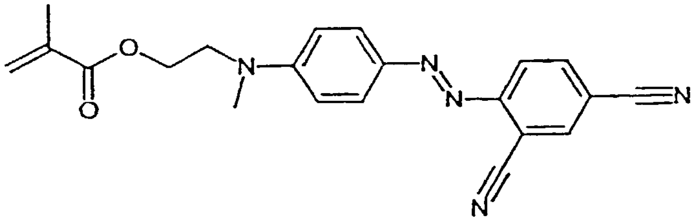

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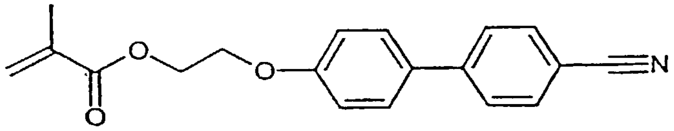

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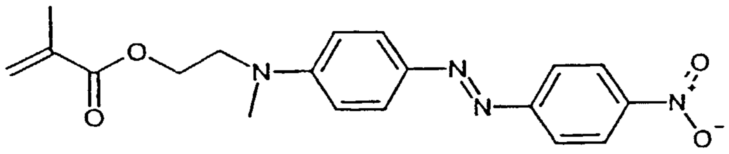

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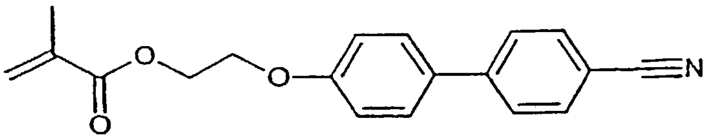

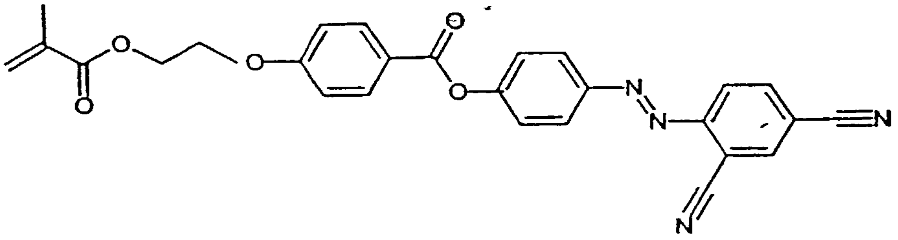

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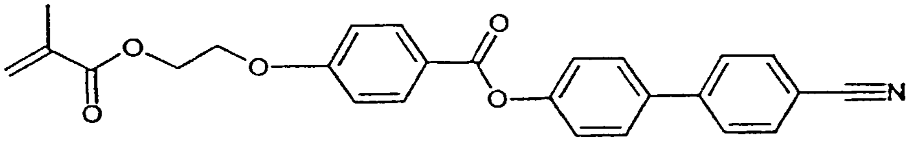

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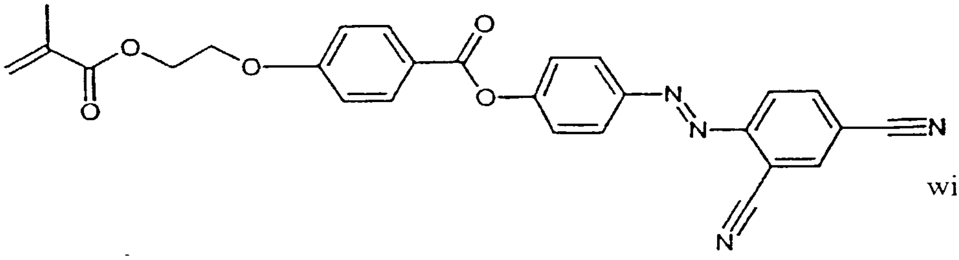

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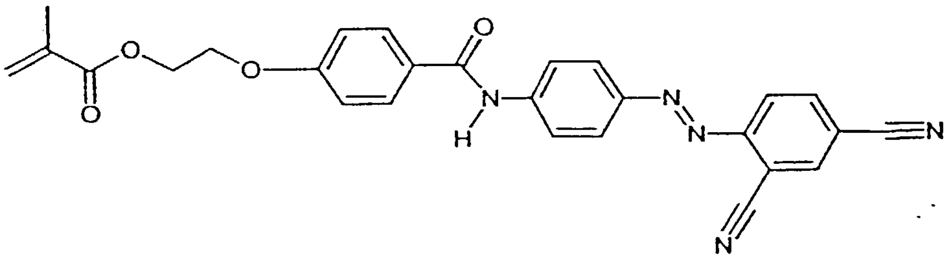

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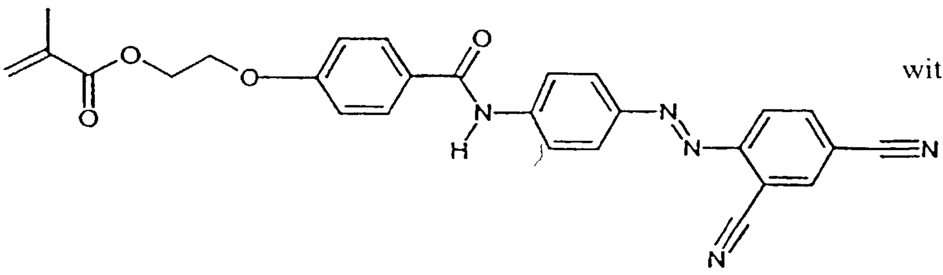

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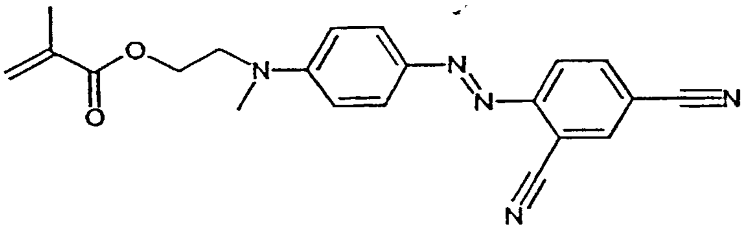

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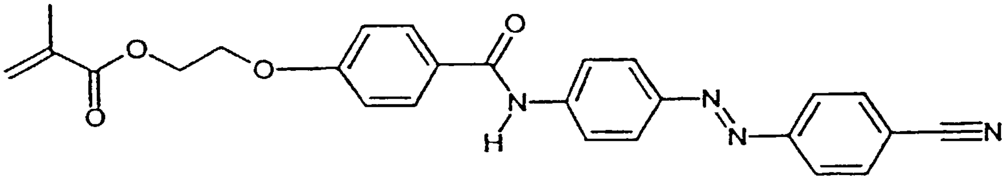

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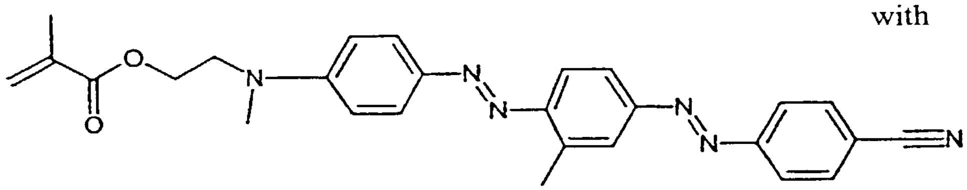

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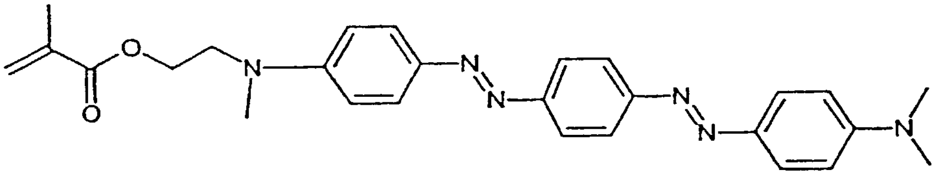

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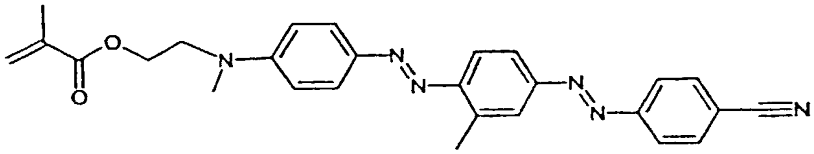

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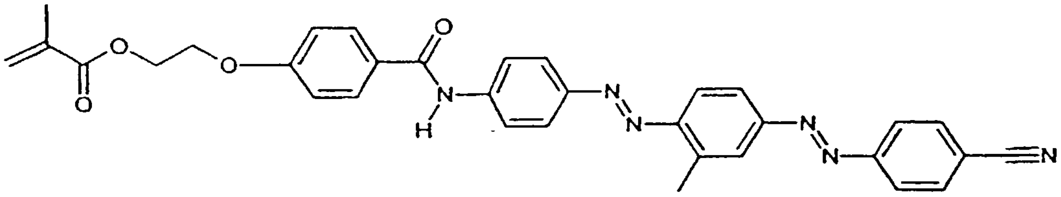

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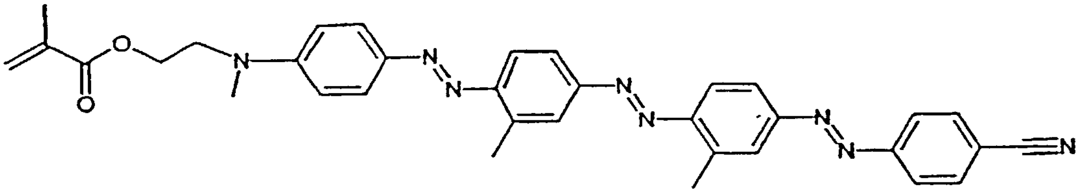

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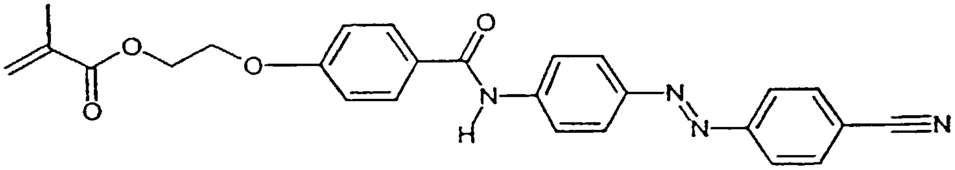

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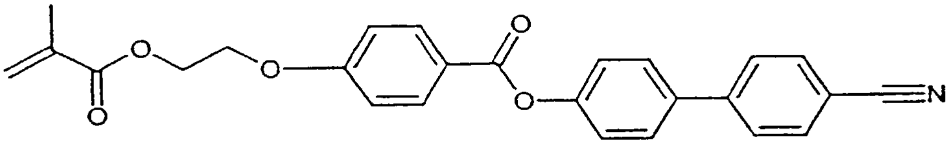

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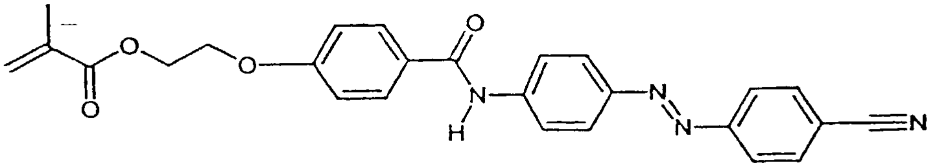

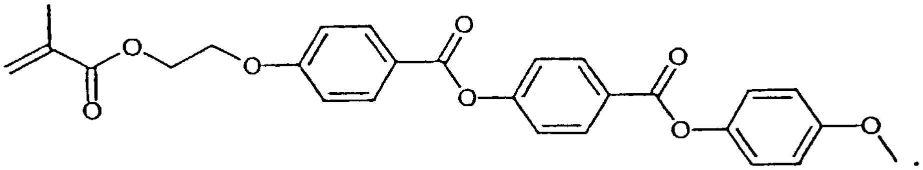

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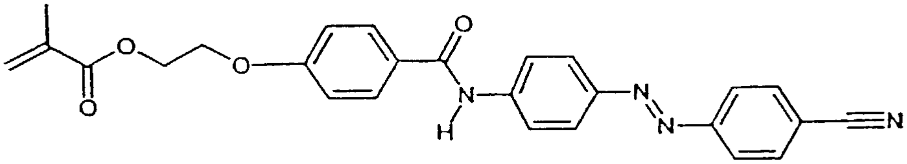

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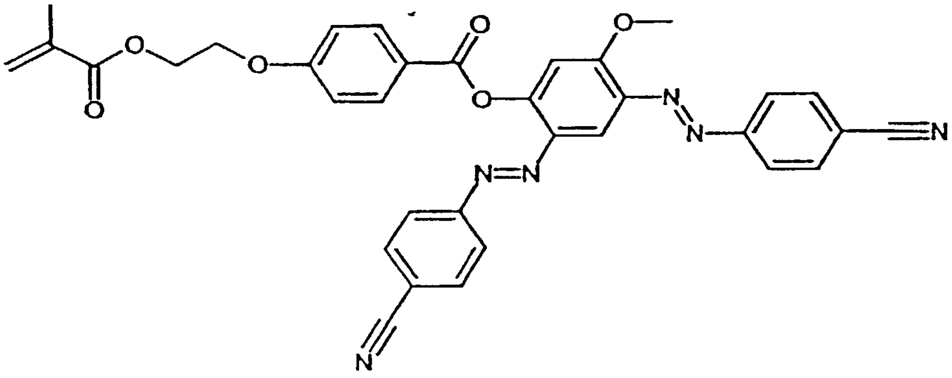

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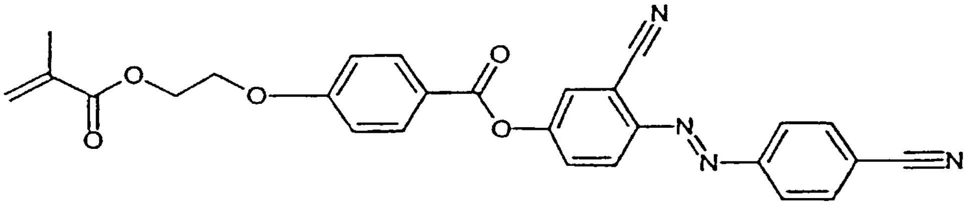

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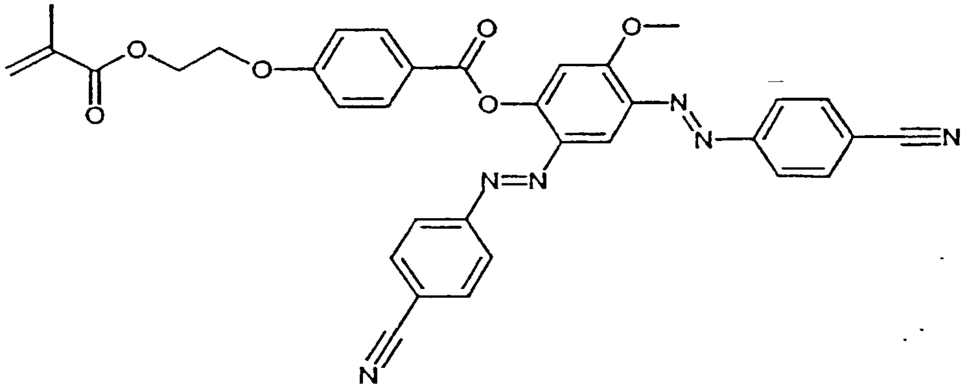

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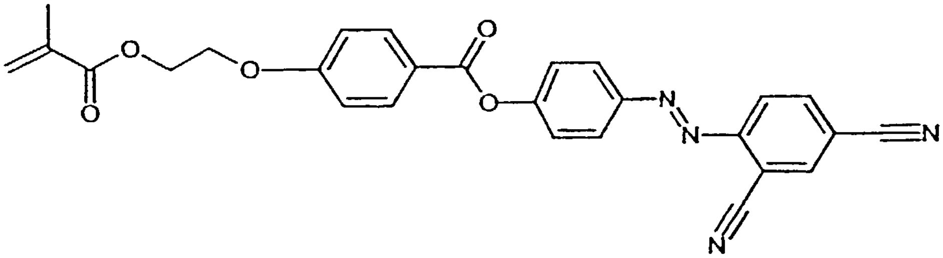

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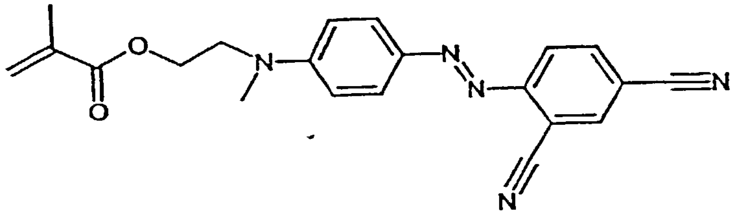

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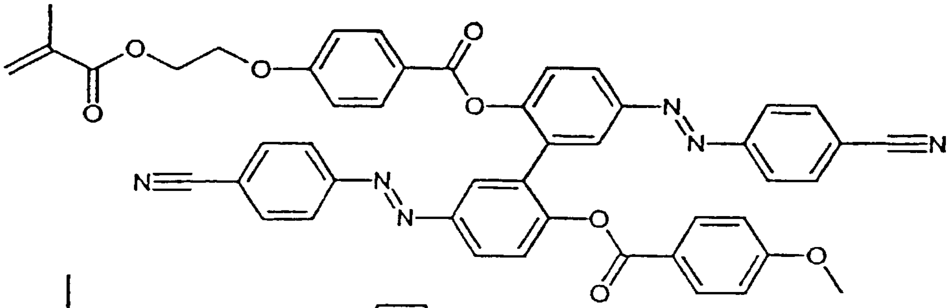

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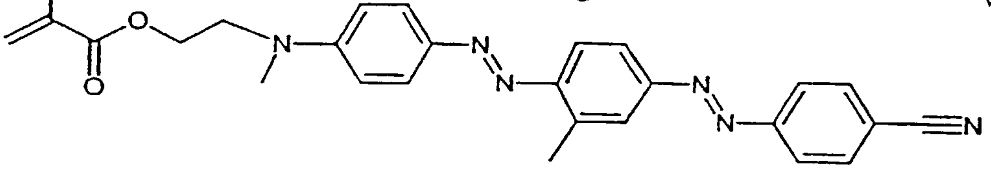
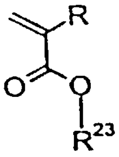


In addition to these functional building blocks (Ia) and (IIa) the oligomers or polymers used in the process according to the invention may also contain building blocks that serve primarily to reduce the percentage content of functional building blocks, in particular the content of dye building blocks. In addition to this objective they may also be responsible for other properties of the oligomers or polymers, for example the glass transition temperature, liquid crystallinity, film-forming properties, etc.

For polyacrylates or polymethacrylates such monomers are acrylic or methacrylic acid esters of the formula (IIIa)



(IIIa),

in which

R denotes hydrogen or methyl and

R^{23} denotes optionally branched C_1- to C_{20}-alkyl or a radical containing at least one further acrylic unit.

Polyacrylates and polymethacrylates used in the process according to the invention then preferably contain as repeating units those of the formulae (Ia), preferably those of the formulae (Ia) and (IIa) or of the formulae (Ia) and (IIIa) or those of the formulae (Ia), (IIa) and (IIIa).

Several of the repeating units of the formula (Ia) and/or of the repeating units of the formulae (IIa) and/or (IIIa) may also be present.

The quantitative ratio between Ia, IIa and IIIa is arbitrary. Preferably the concentration of Ia is, depending on the absorption coefficient of Ia, between 0,1 and 100% referred to the relevant mixture. The ratio of Ia to IIa is between 100:0 and 1:99, preferably between 100:0 and 30:70, and most particularly preferably between 100:0 and 50:50.

The polymers and oligomers used in the process according to the invention preferably have glass transition temperatures T_g of at least 40°C. The glass transition temperature may be measured for example according to B. Vollmer, Grundriß der Makromolekularen Chemie (Outline of Macromolecular Chemistry), pp. 406-410, Springer-Verlag, Heidelberg, 1962.

The polymers and oligomers used in the process according to the invention have a weight average molecular weight of 5,000 to 2,000,000, preferably 8,000 to 1,500,000, measured by gel permeation chromatography (calibrated with polystyrene).

Graft polymers are prepared by the free-radical bonding of monomers (Ia) that carry the dye group of the formulae (I) as well as optionally in addition the bonding of monomers (IIa) that carry the dimensionally anisotropic groups of the formula (II) and/or likewise in addition the bonding of monomers of the formula (IIIa), to oligomeric or polymeric base systems. Such base systems may include the widest possible range of polymers, for example polystyrene, poly(meth)acrylates, starch, cellulose and peptides. The free-radical bonding may take place by irradiation with light or by the use of reagents that produce free radicals, for example tert.-butyl hydroperoxide, dibenzoyl peroxide, azodiisobutyronitrile, hydrogen peroxide/iron(II) salts.

Through the structure of the polymers and oligomers the intermolecular interactions of the structural elements of formulae I with one another or of formulae Ia and IIa with one another may be adjusted so that the formation of liquid crystalline order states is suppressed and optically isotropic, transparent non-scattering films, sheets, plates or tuboids can be produced. On the other hand the intermolecular interactions are still sufficiently strong for a photochemically induced, co-operative, targeted reorientation of the photochrome and the non-photochrome side groups to take place under irradiation with light.

Preferably interactions occur between the side groups of the repeating units of formula Ia or between those of formulae Ia and IIa that are sufficient for the photo-induced configurational change of the side groups of formula I to produce an aligned – so-called co-operative – reorientation of the other side groups Ia and/or II.

All polymers and monomers claimed in the process according to the invention are similarly the subject of the invention. The application also provides for the use of these substances in physical processes. All polymers, oligomers and monomers mentioned in the application and their use for DVD storage systems, optionally using double refraction as a measurement signal, are likewise the subject of the application.

Extremely high values of the optical anisotropy can be induced in the optically isotropic amorphous photochrome polymers (Δn up to 0.4). The expression optically isotropic denotes polymer samples that are not optically opaque, i.e. that exhibit no noticeable light scattering in light scattering experiments with light of a wavelength in the range between 380 and 820 nm.

In this connection it is understood that the ratio of the sum of the scattered light intensity to the incident light intensity is less than 10^{-3}, preferably less than 10^{-4}, particularly preferably less than 10^{-5} and most particularly preferably less than 10^{-6}.

Under the influence of actinic light order states are generated and modified in the polymers or oligomers and the optical properties are thereby modulated.

Polarised light whose wavelength lies in the region of the absorption bands, preferably in the region of the long-wave n-π* bands of the repeating units of the formula Ia, is used as light.

The production of the polymers and oligomers may be carried out according to processes known in the literature, for example according to DE-A 276 297, DE-A 3 808 430, Makromolekulare Chemie **187**, 1327-1334 (1984), SU 887 574, Europ. Polym. **18**, 561 (1982) and Liq. Cryst. **2**, 195 (1987).

Films, sheets, disks and cuboids can be successfully produced without the need for complicated and expensive orientation methods involving external fields and/or surface effects. They can be applied to substrates by spincoating, dipping, casting or other technologically easily accomplished coating processes, can be introduced between two transparent disks by pressing or inflow, or can simply be prepared as a self-supporting material by casting or extrusion. Such films, sheets, disks and cuboids can also be produced from liquid crystalline polymers or oligomers that contain structural elements in the aforedescribed sense, by sudden cooling, i.e. at a cooling rate of >100 K/min, or by rapid removal of the solvent.

Optically transparent materials, for example glass or thermoplastics, preferably polycarbonate, are suitable as substrate materials. If the information is written and read not through the substrate but through the protective layer, then the substrate material no longer has to satisfy the requirement of optical transparency.

It may also be convenient to match the mass density of the covering layer that protects the light-active polymer film against mechanical damage, accurately to the mass density of this polymer film, preferably to a residual difference of less than 0.5 g/cm^3, particularly preferably to less than 0.1 g/cm^3 and most particularly preferably to less than 0.05 g/cm^3. If in fact the flow behaviour of the covering layer is suitably optimised, then this layer completely follows the forced topographical change in the interface between the storage medium and covering layer that occurs during the writing, and no hollow spaces are formed in the interface. In this case however no restoring force exists after the writing, by means of which the written interface topography could be levelled again or otherwise altered. In other words, the information written as interface topography is extremely storage-stable.

In principle any optical imaging system whose image brightness depends largely on the height co-ordinate and/or on the local orientation of the formed interface element is suitable as optical measurement system for reading the topographical information written in the storage medium. For example, measurement methods that are employed in optical profileometers. for example from Rodenstock, or in confocal laser scanning microscopes, for example from Leica Mikrosysteme, may be successfully used, in which connection in the latter case all structural elements that are necessary for scanning the laser beam may of course be omitted.

The contrast mechanism may be based on the principle of interference between beam portions originating from parts of the scanned sample spot lying at different depths, as well as on primarily geometrical-optical effects, for example the inclination contrast: the parts of the surface of the scanned sample spot that are strongly inclined relative to the horizontal deflect the reflected radiation into spatial angular ranges that are no longer covered by the measurement optics system, and the reflection image of the surface-modified sample site becomes dark.

The media that can be subjected to the aforedescribed storage process are built up from at least one substrate material (of plastics, e.g. polycarbonate, PMMA, cyclic polyolefines, polycarbonate copolymers, etc.) and at least one functional covering layer of the aforedescribed functional storage layer. Furthermore additional non-metallic intermediate layers/covering layers may also be arranged between the substrate layers and the function layers, as well as on the function layer itself.

It is already known from the literature that in the case of the materials class comprising photoaddressable polymers, among which the polymers described in more detail above may also be included, surface gratings can be produced when writing holographic gratings (C. Barret. P. Rochon and A. Natansohn. *J. Chem. Phys.* **109** (4), 1505 (1998), D.Y. Kim, S.K. Tripathy, L.Li and J. Kumar, *Appl. Phys. Lett.* **66** (10), 1166 (1995), N. Holme, L. Nikolova, P.S. Ramanujam and S. Hvilsted, *Appl. Phys. Lett.* **70**, 1518 (1997)): the overlapping of two linearly polarised laser beams produces an interference pattern. If a sample is located at the site of this interference pattern, then polymers can be found that follow this light pattern with a modification of the surface.

It has to be said that it is extremely surprising that it is possible just by local illumination with an individual strongly focused light that is guided in a scanning manner over the surface, to change the surface topography locally to such an extent that it can then be reliably read with an optical measurement system without the function layer thereby being destroyed. Such high contrasts were hitherto possible for example only by laser ablation or by vaporisation of for example dye layers in CD-R applications.

Light-induced reorientations of the side chains bonded to the polymer backbone are decisive for the functional capability of the process according to the invention. On absorption of the incident light quanta configurational changes occur in the involved and neighbouring molecules (trans-cis-trans-isomerisation cycles of the azo dyes, co-operative entrainment of the adjacent mesogenic groups). The incident light energy is thus largely used in assisting the molecules to find a new configurational arrangement. The heat that is also released during the absorption appears to assist the rearrangement effect. "Sausage" or "spherical" arch formations that produce a marked drop in the inclination-dependent local signal under optimised optical scanning are thereby formed depending on the guidance of the irradiation.

The process according to the invention enables digital information to be written for example on CD-R-like plastics disks having writing speeds and storage densities similar to those of CD-R, but with the advantage of assured long-term stability, since the readability of the written information can be impaired only by external damage to the storage disk. The written-in structuring in the surface topography can be changed only by heating this layer close to its glass transition temperature. By virtue of the polymer architecture the glass transition temperature is significantly above 100°C, preferably above 150°C, with the result that thermal destruction of stored information can be avoided by proper storage of the storage disk.

A further advantage of the process according to the invention is the significantly improved signal deviation during optical reading of the information, compared to the hitherto commercially used processes. As already mentioned in more detail hereinbefore, the signal deviation is so large that for example the use of a confocal reading method on an additional reflecting layer can be dispensed with.

The invention accordingly describes a storage process in which a storage medium comprising at least one substrate layer and at least one recording layer can be subjected to the storage of digital binary or non-binary information by means of a focused laser beam that can for example be scanned in a continuous or pulsed manner over the sample surface and that can be focused, depending on the layer structure in the case of multiple layers, onto the relevant function layer. Alternatively the laser scanning can be dispensed with if another way of effecting relative movement between the medium and laser spot is employed, for example by rotating the medium.

The layer thickness of the function layer is, depending on the specific absorption (extinction per layer thickness) of the layer in a range between 0.05 and 100 µm, preferably between 0.1 and 10 µm, and most particularly preferably between 0.1 and 2 µm. The layer thickness may be determined either from the specific absorption of the function layer measured in a preceding measurement process and from the extinction of the function layer, or mechanically (by damaging the layer and scanning with a profileometer, for example from the Tencor Company.

The layer thickness of the at least one protection layer is in a range between 0.1 and 1000 µm, preferably between 0.1 and 100 µm, and particularly preferably between 0.5 and 10 µm.

At the wavelength of the laser that is used to write the surface topography, the optical density of the function layer is in a range between 0.3 and 20, preferably between 0.5 and 10, particularly preferably between 0.7 and 8, and most particularly preferably between 1 and 5.

The intensity of the laser that is used for the writing is in the output range of commercial laser diodes: intensities of between 150 µW and 100 mW, preferably between 500 µW and 50 mW, particularly preferably between 750 µW and 30 mW, and most particularly preferably between 1 mW and 20 mW, are used. If the same laser is also used for reading, then its intensity must be less than the intensity used for writing, preferably by a factor of 10, particularly preferably by a factor of 100, and most particularly preferably by a factor of 1000.

If a laser whose wavelength does not lie in the absorption range of the dyes of the polymers is chosen to read the information, then the output density of the laser beam may be even higher than that of the writing laser. Since the maximum permissible reading speed in the case of present- day commercial systems is already limited by the quantum noise of the measurement signal, this means that in the case of a system according to the invention the reading speed can be significantly raised by using a high output reading laser.

Depending on the wavelength of the laser that is used, the laser beam is focused by commercially available and/or specially optimised lens systems and object lenses.

The dimension of the laser beam (full half-value width) is in a range between 300 nm and 8 μm, preferably between 300 nm and 950 nm, particularly preferably between 350 nm and 800 nm, and most particularly preferably between 380 nm and 650 nm.

Furthermore, this effect should also be achieved in the optical near field. In this case the dimension is less than 100 nm, preferably less than 50 nm, and most particularly preferably less than 10 nm.

In the process according to the invention a depression of at least 10 nm, particularly preferably of at least 50 nm, and most particularly preferably of at least 100 nm, is preferred as change in the surface topography of the light-active layer of the storage medium.

The depression produced in the storage medium in the process has a width in one direction, measured on the original surface, of less than 10 μm, preferably less than 5 μm and particularly preferably less than 1 μm.

In the preferred process according to the invention a signal deviation of at least carrier/noise = 20 dB, particularly preferably at least 40 dB and most particularly preferably at least 60 dB is written in the storage medium.

Carrier noise ratio is defined as follows: $C/N = 20 \log (I_{signal}/I_{noise}$, I_{signal} = measured detection signal and I_{noise} = noise level.

The focused laser beam is guided for example by deflecting the laser beam by means of a mirror having a controllable and adjustable angular setting (Scanoptik) or by rotating the substrate under the focused laser spot. The relative velocity between the medium and laser spot is in a range between 0.01 m/sec and 600 m/sec, preferably between 0.2 m/sec and 100 m/sec, particularly preferably between 0.5 m/sec and 75 m/sec and most particularly preferably between 1 m/sec and 60 m/sec.

In order to detect the light-induced surface modification, an arrangement identical to that also used for the writing may for example be used. For this purpose the output density of the writing laser may for example be reduced. Alternatively another laser source may for example also be used, preferably lasers that emit at longer wavelengths than the writing laser. In this case the reading wavelengths are preferably at least 20 nm, particularly preferably 50 nm and most particularly preferably 100 nm greater than the writing wavelengths.

Dynamic exposure experiments may be carried out in a suitable recorder arrangement on two-dimensional structures. To this end light pulses from a laser (the so-called writing laser) focused onto the recording layer are used, in order to write information locally on a circular or spiral track. The wavelength of the writing laser is in the absorption range of the dye molecules of the recording material, preferably at wavelengths between $\lambda = 380$ nm and $\lambda = 820$ nm, particularly preferably at wavelengths between $\lambda = 385$ nm and $\lambda = 780$ nm, and most particularly preferably at wavelengths between $\lambda = 385$ nm and $\lambda = 660$ nm.

The substrate coated with the recording material rotates at 60 to 60000 revs/min, preferably at 100 to 10000 revs/min, particularly preferably at 200 to 1000 revs/min. At a pulse duration of the writing laser of 4 ns to 10 µs, preferably 10 ns to 1 µs, the pulses are focused at spatial distances of 0.3 to 50 µm, preferably 0.3 to 10 µm, onto the recording layer.

The initial output of the modulable writing laser is in the range from 0.15 to 100 mW, preferably between 0.5 and 50 mW, particularly preferably between 0.75 and 30 mW, and most particularly preferably between 1 mW and 20 mW. The writing laser beam is focused onto the recording layer, which was applied from solution onto a mirror-coated substrate. The diameter of the focal point is 0.30 to 8 µm, preferably 0.30 to 0.95 µm, particularly preferably 350 nm to 800 nm, and most particularly preferably 380 nm to 650 nm. In the near field the focal point is less than 100 nm, preferably less than 50 nm, and most particularly preferably less than 10 nm. In the laser light focal point output density of up to 100 MW/cm^2 are reached. The energy density of a pulse is in the range from 1 mJ/cm^2 to 100 J/cm^2. The polarisation of the writing laser is preset by conventional polarisation systems (quartz optics, LC components) and is *inter alia* linearly or circularly polarised, preferably linearly polarised.

A suitable modulator converts a computer-generated voltage pulse sequence into an intensity pattern that locally changes the anisotropy existing in the recording film.

It has been experimentally found that the light pulses of the writing laser have, depending on the energy, different effects on the polymer layer:

1. For small pulse energies, changes are induced by the light pulses in the level of the double refraction of the recording material, as already described in Le A 31 135. These changes in the molecular orientation distribution are induced by photons and/or thermally.

2. With increasing pulse energy it was found that the light from the writing laser has a second effect on the recording layer: surprisingly a modification of the surface of the recording material is produced. The laser pulse generates a crater-like shape having a central depression and edge accumulations. This surface structure has maximum lateral dimensions that exceed the diameter of the focal point by 10 to 30%. The profile depth increases with the pulse energy and can approach the value of the layer thickness, and may typically be up to 60% to 80% of the layer thickness.

The threshold for the energy density of a light pulse at which the surface effects described in Point 2 exceed the typical roughness of a surface of the recording layer of 2 to 6 nm, lies between 10 mJ/cm^2 and 100 J/cm^2, preferably between 20 mJ/cm^2 and 10 J/cm^2 and particularly preferably between 50 mJ/cm^2 and 1 J/cm^2.

As recording medium a layer arrangement is used that comprises at least one substrate layer and at least one recording layer.

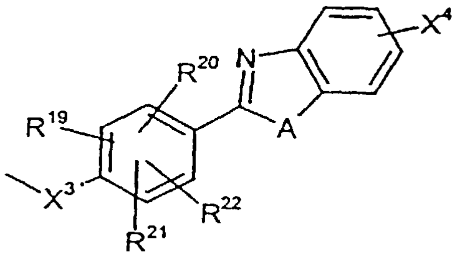
The storage media are prepared for example by spincoating a solution of the polymer onto a substrate material. For this purpose conventional solvents such as THF or DMF are employed.

The invention also describes the use of such a treated two-dimensional structure in the area of optical components, for example as diffraction elements.

The process according to the invention furthermore includes the use of polymers that preferably contain at least one side chain of the formula (I).

in which

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula



$X^{3'}$ denotes –N=N- or –CO-NH-

and the other radicals have the aforementioned general preferred and particularly preferably meanings.

These polymers are likewise a subject of the invention.

Preferably

$X^{3'}$ denotes –N=N- or –CO-NH-,

X^4 denotes hydrogen or methyl,

A denotes S,

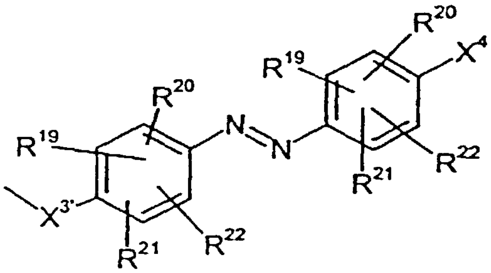
R^{19} to R22 independently of one another denote hydrogen, methyl or methoxy

and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

In the process according to the invention the use of polymers that contain at least one side chain of the formula (I) is furthermore preferred,

in which

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula



$X^{3'}$ denotes –O-, -(SO_2)-, -(C=O)-, -(N-R^5)-, -(CO-NR^5)- or -C(R^6R^7)-

and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

These polymers are likewise the subject of the invention.

Preferably

$X^{3'}$ denotes –O-, -(SO_2)-, or -(N-R^5)-,

X^4 denotes hydrogen, C_1- to C_4- alkoxy, Di-C_1- to C_4-alkylamino, C_1-, to C_4-alkanoylamino, benzoylamino, cyano or nitro,

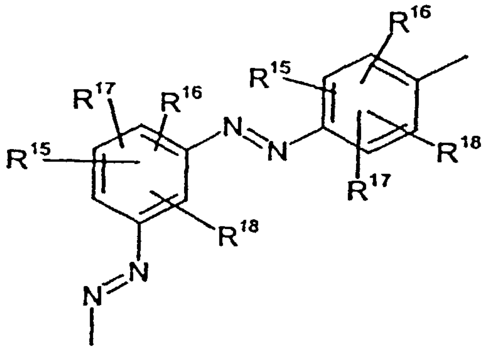
R^{19} to R^{22} independently of one another denote hydrogen, methyl, methoxy or cyano,

and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

In the process according to the invention the use of polymers that contain at least one side chain of the formula (I) is furthermore preferred,

in which

-($X^{2'}$-Ar^2)$_y$- denotes a bivalent radical of the formula



and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

These polymers are also the subject of the invention.

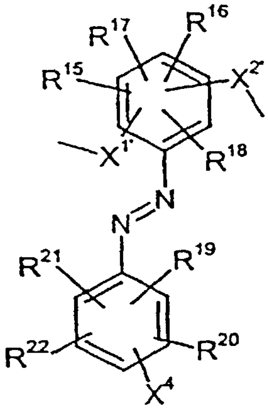
Preferably

R^{15} to R^{18} independently of one another denote hydrogen, methyl, methoxy or cyano, wherein the meanings in the two rings may be different.

In the process according to the invention the use of polymers that contain at least one side chain of the formula (I) is furthermore preferred,

in which

$-(X^{1'}-Ar^{1})-X^{2'}-$ denotes a bivalent radical of the formula



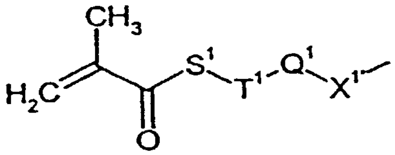
wherein $X^{1'}$ and $X^{2'}$ are in the m- or p-position relative to one another and $X^{1'}$ and the azo group are in the o- or p-position relative to one another,

and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

These polymers are also the subject of the invention.

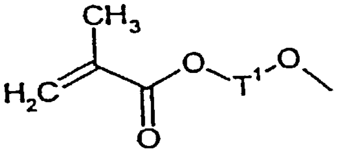
Preferably

$X^{1'}$ denotes a radical of the formula

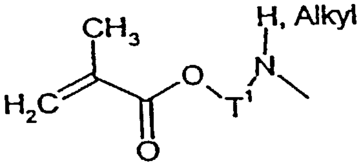

CH3
H2C
O
S1
T1
Q1
X1'

,

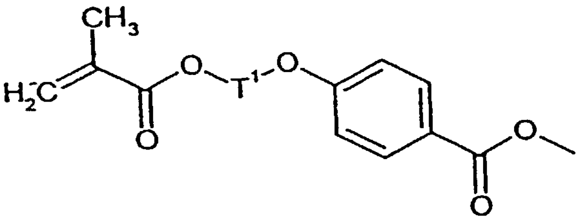
in particular a radical of the formulae


CH3
H2C
O
O
T1
O

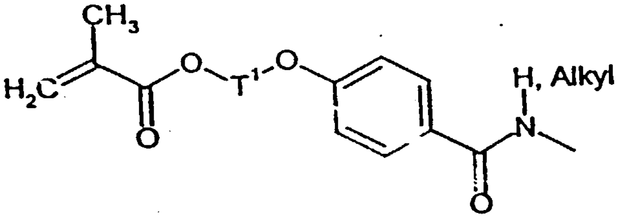
,


CH3
H, Alkyl
N
H2C
O
T1
O

,


CH3
H2C
O
T1
O
O
O
O

or

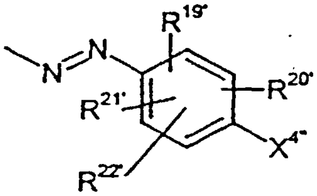

CH3
H2C
O
T1
O
O
H, Alkyl
N
O

,

$X^{2'}$ denotes –N=N- or -CO-NH-,

X^4 denotes hydrogen, C_1- to C_4-alkoxy, Di-C_1- to C_4-alkylamino, C_1- to C_4-alkanoylamino, benzoylamino, cyano or nitro, wherein X^4 in the p-position to the azo group is particularly preferred,

R^{15} to R^{22} independently of one another denote hydrogen, methyl, methoxy or cyano, wherein one of the radicals R^{19} to R^{22} may denote a radical of the formula



which is particularly preferably in the m- or p-position relative to the azo group,

in which

$X^{4''}$ denotes hydrogen, C_1- to C_4-alkoxy, Di-C_1- to C_4-alkylamino, C_1- to C_4-alkanoylamino, benzoylamino, cyano or nitro and

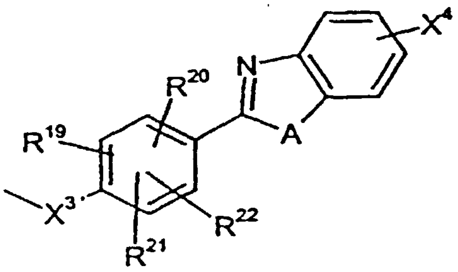
$R^{19'}$ to $R^{22'}$ independently of one another denote hydrogen, methyl, methoxy or cyano, and

S^1, T^1 and Q^1 have the aforementioned general, preferred and particularly preferred meanings.

The present invention also provides monomers of the formula (Ia),

in which

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula



$X^{3'}$ denotes –N=N- or –CO-NH-

and the other radicals have the aforementioned general, preferred and particularly preferred meanings,

as well as their use in the production of polymers of the formula (I).

Preferably

$X^{3'}$ denotes –N=N- or –CO-NH-,

X^4 denotes hydrogen or methyl,

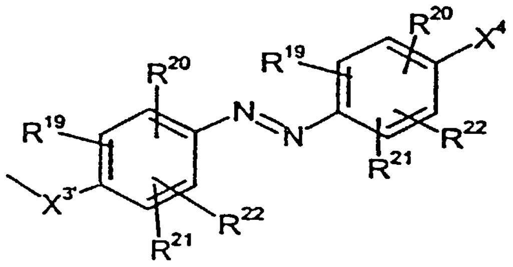
A denotes S,

R^{19} to R^{22} independently of one another denote hydrogen, methyl or methoxy

and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

The invention also provides monomers of the formula (Ia) in which

$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula



$X^{3'}$ denotes -O-, -(SO$_2$)-, -(C=O)-, -(N-R^5)-, -(CO-NR^5)- or -C(R^{6}R^7)-

and the other radicals have the aforementioned general, preferred and particularly preferred meanings,

as well as their use in the production of polymers of the formula (I).

Preferably

$X^{3'}$ denotes –O-, -(SO$_2$)-, or -(N-R^5)-,

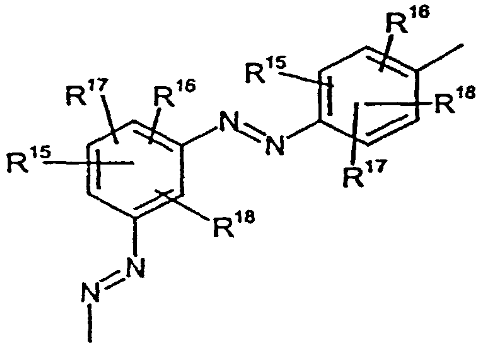
X^4 denotes hydrogen, C_1- to C_4- alkoxy, Di-C_1- to C_4-alkylamino, C_1-, to C_4-alkanoylamino, benzoylamino, cyano or nitro,

R^{19} to R^{22} independently of one another denote hydrogen, methyl, methoxy or cyano,

and the other radicals have the aforementioned general, preferred and particularly preferred meanings.

The invention also provides monomers of the formula (Ia) in which

$-(X^{2'}-Ar^2)_y-$ denotes a bivalent radical of the formula


R16
R15
R17
R16
R18
R15
R17
R18
N
N
N
N

and the other radicals have the aforementioned general, preferred and particularly preferred meanings,

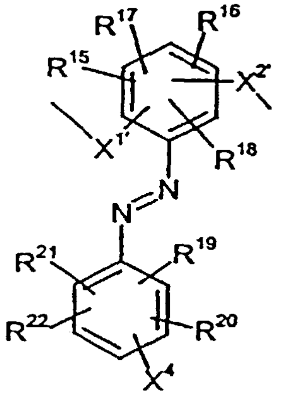
as well as their use for producing polymers of the formula (I).

Preferably

R^{15} to R^{18} independently of one another denote hydrogen, methyl, methoxy or cyano, wherein the meanings in the two rings may differ.

The invention also provides monomers of the formula (Ia), in which

$-(X^{1'}-Ar^1)-X^{2'}$ denotes a bivalent radical of the formula

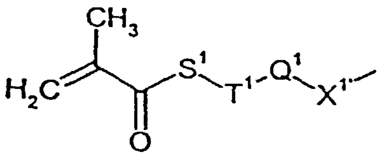

R17
R16
R15
X2'
X1'
R18
N
N
R21
R19
R22
R20
X4

wherein $X^{1'}$ and $X^{2'}$ are in the m- or p-position relative to one another and $X^{1'}$ and the azo group are in the o- or p-position relative to one another,
and the other radicals have the aforementioned general, preferred and particularly preferred meanings,

as well as their use for producing polymers of the formula (I).

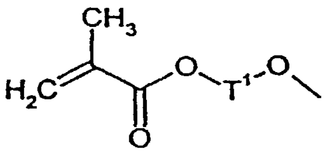
Preferably

$X^{1'}$ denotes a radical of the formula

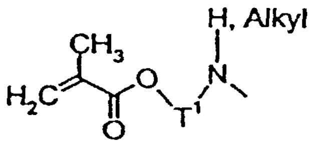

CH3
H2C
O
S1
T1
Q1
X1'

,

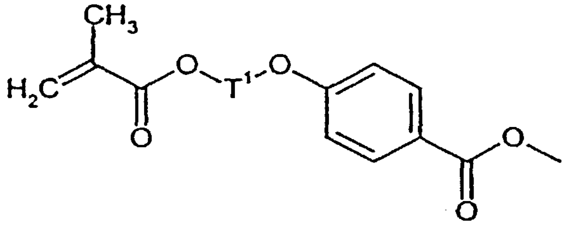
in particular a radical of the formulae


CH3
H2C
O
O
T1
O

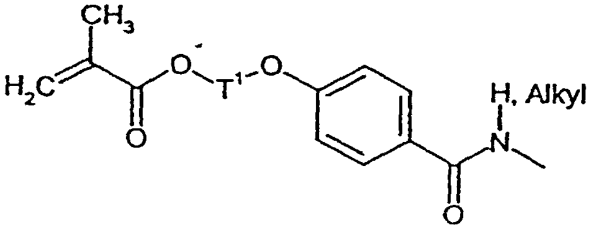
,


H, Alkyl
CH3
H2C
O
O
T1
N

,


CH3
H2C
O
O
T1
O
O
O

or

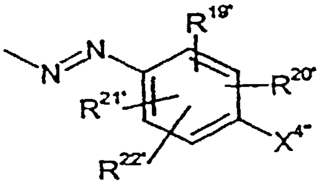


,

$X^{2'}$ denotes –N=N- or –CO-NH-,

X^4 denotes hydrogen, C_1- to C_4-alkoxy, Di-C_1- to C_4-alkylamino, C_1- to C_4-alkanoylamino, benzoylamino, cyano or nitro, wherein X^4 is particularly preferably in the p-position relative to the azo group,

R^{15} to R^{22} independently of one another denote hydrogen, methyl, methoxy or cyano, wherein one of the radicals R^{19} to R^{22} may denote a radical of the formula



that is particularly preferably in the m- or p-position relative to the azo group,

in which

$X^{4''}$ denotes hydrogen, C_1- to C_4-alkoxy, Di-C_1- to C_4-alkylamino, C_1- to C_4-alkanoylamino, benzoylamino, cyano or nitro, and

$R^{19'}$ to $R^{22'}$ independently of one another denote hydrogen, methyl, methoxy or cyano, and

S^1, T^1 and Q^1 have the aforementioned general, preferred and particularly preferred meanings.

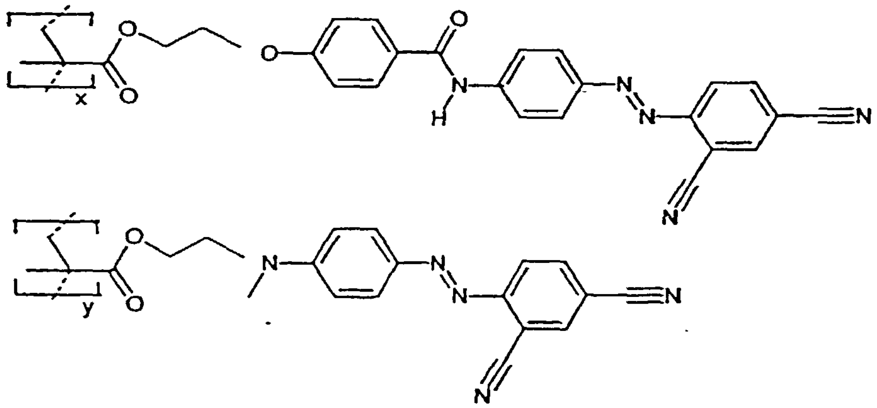
The process according to the invention is described in more detail hereinafter with the aid of the following examples.

Examples

Example 1

Dynamic writing experiments in an adapted recording unit

Dynamic exposure experiments were carried out in a fully automated manner with a recorder described in more detail hereinbelow, on a mirror-coated substrate wetted with a (250±30) nm thick layer of polymers of the formulae



A double refraction of 0.1 was written two-dimensionally in a recording layer with a (describe the device accurately), the polarisation direction of the pre-exposure being 45° to the radius. The substrate rotated at 600 revs/min. At a pulse duration of 10 µs and a computer-controlled adjustable track radius of 1.6 to 4.9 cm, the memory locations were then 10 to 35 µm apart.

A diode-pumped Nd:YAG laser (from Coherent) was used as writing laser, whose second harmonic (wavelength 532 nm) passed through an acousto-optical modulator (from Isomet) and was coupled via a fibre into the recorder. The emitting power after the fibre was a maximum of 18 mW. Alternatively a LASER diode could also be used, which is directly modified and in this way generates variously intensive LASER pulses. The writing beam passed through a dichroitic beam splitter and was focused onto the recording layer. The diameter of the focal point was (7±1) µm. The pulse energy was varied in a computer-controlled manner in 1000 equidistant steps of 0.1 to 100 J/cm^2. The writing laser was polarised at 45° to the radial direction and at 90° to the pre-illumination direction of the PAP layer. The acousto-optical modulator converted a computer-generated voltage pulse sequence into an intensity pattern that gradually locally extinguished the anisotropy existing in the polymer film.

In the recorder a semiconductor laser diode (reading laser) of wavelength 670 nm (output 20 mW) was coupled via the dichroitic beam splitter laterally into the writing beam path and focused onto the information carrying track of the recording layer. The diameter of the focal point was 11 µm. The light from the reading laser was reflected at the aluminium layer of the substrate and passed twice through the recording layer. A polarisation-dependent beam splitter decoupled the depolarised portions of the back-reflected light sideways, so that it could be detected by a photoelectric cell. The grey levels were made visible electronically using a high-pass unit. The height of the intensity level was adjusted via the energy of the respective writing pulse.

It was found that with increasing pulse energy there was a modification of the surface of the recording layer. The crater-like shape that the laser pulse had created extended 9 µm in the radial direction. The profile depth increased with the pulse energy. Up to pulse energies of 10 J/cm^2 (intensity 1MW/cm^2) the modifications had a maximum size of 3 nm. This corresponds to the typical roughness of a polymer layer deposited by centrifugation from solution. The modification of the recording layer was so marked at the maximum available energy of 100 J/cm^2 (intensity 10MW/cm^2) that its shape could easily be resolved using an atomic force microscope (AFM). The central depression was (70±10) nm. (30±5) nm high accumulations could be observed at the edge.

Example 2

Functional capability of the writing and reading processes

The functioning of the aforedescribed storage process may be illustrated for example by means of a confocal laser scanning microscope (CLSM). A commercial item of equipment from Leica (TCS/NT equipment) was used in this example. This CLSM is a microscope in which the laser can furthermore be modulated and/or pulsed with the aid of an AOM. The contrast-producing mechanisms were discovered by means of REM and AFM investigations and compared with the confocal contrast of the CLSMs. The CLSM was operated with a 16x object lens. A wavelength of 488 nm was used to write the information. The output on the sample surface was 150 µW, and the diameter of the laser spot was 940 nm. The output density at the sample site was calculated therefrom as:

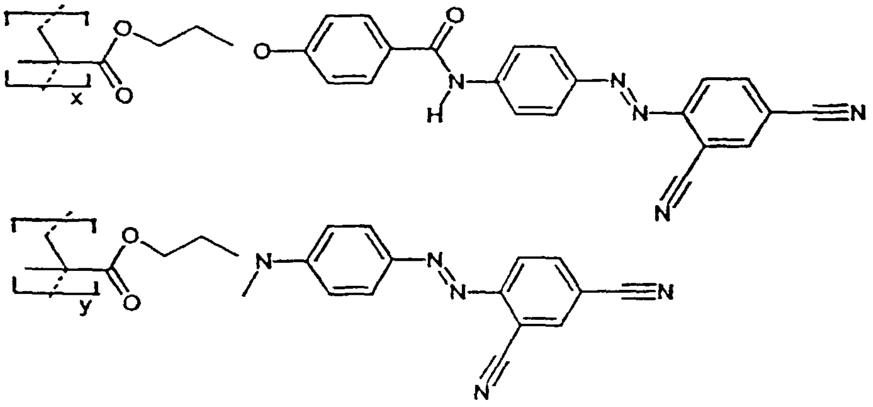
$$P = 2.16 \times 10^7 \text{ mW/cm}^2$$

The duration of the scanning of a line was 2.2 ms, of which 0.77 ms represented the actual scanning of the line (remainder: cusp points, reflected light, etc.). The lateral dimension of the line could be fixed by the choice of visual field, the smallest visual field being 20 µm. On enlarging the visual field, both the time required for scanning a line (0.77 ms) as well as the output density on the sample remained the same, and only the scanning range, i.e. the length of the line, increased. This accordingly leads to an increase in the scanning rate, which effectively means a reduction of the residence time of the laser on a particular polymer point.

In order to effect the writing, the argon laser (488 nm) was repeatedly switched on and off within the scanned line by means of an AOM. The scanning of the line could be repeated with a high degree of precision in successive experiments without the positions of the individual pixels being significantly smeared.

The written lines were detected with an HeNe laser. This laser has on the one hand the great advantage that, since its wavelength lies outside the absorption wavelengths of the polymers, it simply makes diffractive and no absorbing contributions to the detected signal. Secondly, this wavelength is not able to induce any noticeable molecular reorientations, which thereby ensures that the measured contrast ratios are solely produced by the irradiation with the argon laser.

A ca. 1 μm thick sample of the polymer



was used.

For the process according to the invention the formation of this surface-modification constitutes the actual contrast-producing mechanism.

Example 3

Storage stability

The sample in which a surface modification was written in Example 1 was stored for 1 month at 160°C. After this storage the sample was investigated again using a confocal microscope. The previously written surface modification was found to be unchanged when examined under both CLSM and AFM.

Example 4

Comparison with confocal contrast in CD-R

A commercial CD-R (KODAK, Digital Science CD-R, 650 MB, 74 min) was written with a commercially available CD-burner (TEAC Company, CD-R55SK, CD-writer). The written CD was investigated in a CLSM from LEICA (TCS/NT) at a wavelength of 632 nm in a visual field of 20 μm x 20 μm. The written pits could be clearly recognised. The difference of the intensity values measured in the confocal reflection mode between unwritten and written regions was compared with the difference of the intensities along the surface topographies written in Example 1: under identical settings the confocal contrast of the surface topographies written in Example 1 was greater by a factor of 2 to 3 than the contrast along the pits of the burnt CD.

Example 5

Exposure through the covering layer

A ca. 10 μm thick UV-hardening covering layer (BAYER, Roskydal 2265, applied by spincoating at 3000 revs/min) was applied to the polymer on a sample produced as described in Example 1 and was exposed for 15 seconds under a commercially available lamp to cure the UV lacquers. A double refraction was then produced in the sample as described in Example 1, following which a pulse sequence was written, likewise as described in Example 1. Confocal investigations showed that, despite the covering layer, the surface topographies described in Example 1 could still be observed, and furthermore without the occurrence of any hollows, bubbles or similar defects at the interface between the storage medium and the covering layer.

Patent Claims

1. Process for the optical writing of optically readable digital information in a two-dimensional extended storage medium, characterised in that on account of the optical writing process the surface topography of the storage medium is suitable and sufficiently modified for the optical reading process, and more specifically without substantial portions of the detected signal resulting from a degradation and/or a physical or chemical modification of the areas adjacent to the absorber layer.

2. Process according to claim 1, characterised in that polymer films are used as storage medium.

3. Process according to claim 1, characterised in that a multi-layer disk is used as storage medium, which comprises at least one mechanically sufficiently stable substrate, at least one polymer film forming the light-active layer, and a covering layer.

4. Process according to one or more of the preceding claims, in which a storage medium is used and the light-active layer predominantly comprises oligomers and/or polymers containing dyes that orientate under the action of light, preferably amorphous polymers, particularly preferably side group polymers.

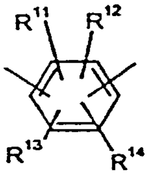
5. Process according to one or more of the preceding claims, characterised in that a polymer film whose mass density is closely matched to that of the light-active layer is used as covering layer.

6. Process according to one or more of the preceding claims, wherein as light-active polymer films side-chain polymers, optionally block polymers and/or graft polymers are used, to which dyes are bound as side chains via a STQ-

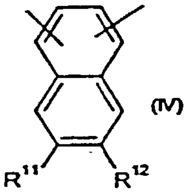
spacer (formula I) and dimensionally anisotropic groups are likewise bound via a STQ-spacer (formula II), wherein formula I has the structure

$$—S^1—T^1—Q^1—X^{1'}—Ar^1—\left(X^{2'}—Ar^2\right)_y—\left(X^{3'}—Ar^3\right)_z—X^4 \qquad \text{(I)}$$

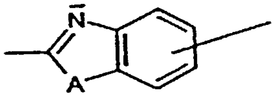
-Ar¹- where =


R11
R12
R13
R14

(III) or

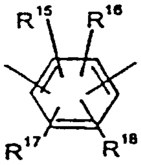


(IV) or

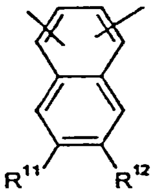


(V)

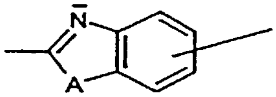
-Ar²- where =


R15
R16
R17
R18

(VI) or

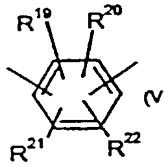


(IV) or

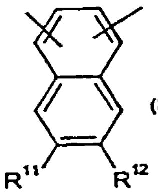


(V)

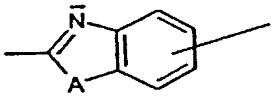
-Ar³- where =


R19
R20
R21
R22

(VII) or



(IV) or



(V)

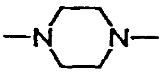
in which

y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings, if y and/or z denote 2, A denotes O, S or N-C_1- to C_4-alkyl,

Q^1 and Q^2 independently of one another denote -O-, -S-, -(N-R^5)-, -C(R^6R^7)$_p$, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -(C=NR^8)-, -(CNR^8-NR^5)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote -(CH_2)$_p$-, wherein the chain may be interrupted by -O-, -NR^9-, or -$OSiR^{10}{}_2O$- and may be substituted by methyl,

S^1 and S^2 independently of one another denote a direct bond, -O-, -S- or -NR^9-,

P denotes an integer from 2 to 12, preferably 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl, ethyl, or propyl ,

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen or a non-ionic substituent,

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, -COO-C_1- to C_4-alkyl or $X^{4'}$-R^4,

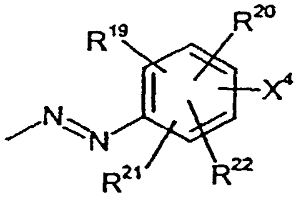
$X^{1'}$, $X^{2'}$ $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -S-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-, -(CO-O)-, -(CO-NR^5)-, -(SO_2)-, -(SO_2-O)-, (SO_2-NR^5)-, or -(CNR^8-NR^5)- and

$X^{2'}$ and $X^{3'}$ may in addition denote -(C=NR^8)-, -(N=N)- and at least one of the groups $X^{2'}$ or $X^{3'}$ denotes -N=N-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-, C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O), C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2), C_2- to C_{20}-alkenyl-(SO_2)- or C_6- to C_{10}-aryl-(SO_2), wherein

by the term non-ionic substituents are understood halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_1- C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O)-, C_1- to C_{20}-alkyl-NH-(C=O)-, C_6 to C_{10}-aryl-NH-(C=O)- or a radical of the formula



(VIII)

and the alkyl, cycloalkyl, alkenyl and aryl radicals in turn may be substituted by up to 3 radicals from the group comprising halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl or C_6- to C_{10}-aryl, and the alkyl and alkenyl radicals may be straight-chain or branched, and

by the term halogen is understood fluorine, chlorine, bromine and iodine, in particular fluorine and chlorine,

and formula II is described by

$$—S^1—T^1—Q^1—X^{1'}—Ar^1—\left(X^{2'}—Ar^2\right)_y—\left(X^{3'}—Ar^3\right)_z—X^4 \qquad \text{(II)}$$

wherein the above substituent definitions (formula I) are also valid for formula II, with the proviso that none of the groups $X^{2'}$ or $X^{3'}$ may denote -N=N- and R^{11} to R^{22} may not denote a radical of the formula (VIII).

7. Process according to claim 6, characterised in that the dye side groups I are used, wherein substituents and formulae have the meanings defined in claim 6, and in addition

Ar^1 denotes a radical of the formula (III),

Ar^2 denotes a radical of the formula (VI),

Ar^3 denotes a radical of the formulae (VII) or (V),

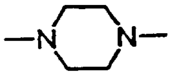
y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and $X^{3'}$ and Ar^3 may have different meanings if y and/or z denote 2,

A denotes O or S,

Q^1 and Q^2 independently of one another denote -O-, -(N-R^5)-, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote $-(CH_2)_p-$ wherein the chain may be interrupted by -O-, $-NR^9-$, or $-OSiR^{10}{}_2O-$ and may be substituted by methyl,

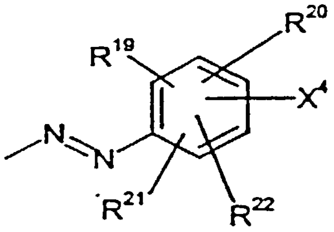
S^1 and S^2 independently of one another denote a direct bond, -O-, -S-, or $-NR^9-$

p denotes an integer from 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl or ethyl,

R^{10} denotes methyl or ethyl.

R^{11} to R^{22} independently of one another denote hydrogen, halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_1- to C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O)-, C_1- to C_{20}-alkyl-NH-(C=O)-, C_6- to C_{10}-aryl-NH-(C=O)- or a radical of the formula



(VIII)

X^4 denotes hydrogen, halogen, cyano, nitro, CF_3, CCl_3, -COO-C_1 to C_4-alkyl or $X^{4'}$-R^4,

$X^{1'}$, $X^{2'}$ $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-, -(CO-O)-, -(CO-NR^5)-, -(SO_2)- or (SO_2-O)- and

$X^{2'}$ and $X^{3'}$ may in addition denote -(N=N)- and at least one of the groups $X^{2'}$ or $X^{3'}$ denotes -N=N-,

R^4, R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl, or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-, C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2)-, C_2- to C_{20}-alkenyl-(SO_2)-, or C_6- to C_{10}-aryl-(SO_2)-.

and dimensionally anisotropic side groups II are used wherein substituents and formulae have the meanings defined in claim 6, and in addition

Ar^1 denotes a radical of the formula (III),

Ar^2 denotes a radical of the formula (VI),

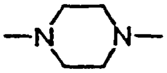
Ar^3 denotes a radical of the formulae (VII) or (V),

y denotes 1 or 2,

z denotes 0, 1 or 2 and

$X^{2'}$ and Ar^2 and/or $X^{3'}$ and Ar^3 may have different meanings if y and/or z denote 2, A denotes O or S,

Q^1 and Q^2 independently of one another denote -O-, -(N-R^5)-, -(C=O)-, -(O-CO)-, -(NR^5-CO)-, -(SO_2)-, -(O-SO_2)-, -(NR^5-SO_2-)-, -O-C_6H_5-COO- or a bivalent radical of the formula



T^1 and T^2 independently of one another denote -(CH_2)$_p$-, wherein the chain may be interrupted by -O-, -NR^9-, or -$OSiR^{10}{}_2O$- and may be substituted by methyl,

S^1 and S^2 independently of one another denote a direct bond, -O-, -S-, or -NR^9-

p denotes an integer from 2 to 8, in particular 2 to 4,

R^9 denotes hydrogen, methyl or ethyl,

R^{10} denotes methyl or ethyl,

R^{11} to R^{22} independently of one another denote hydrogen, halogen, cyano, nitro, C_1- to C_{20}-alkyl, C_1- to C_{20}-alkoxy, phenoxy, C_3- to C_{10}-cycloalkyl, C_2- to C_{20}-alkenyl, C_6- to C_{10}-aryl, C_1- to C_{20}-alkyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_1- to C_{20}-alkyl-(C=O)-O-, C_1- to C_{20}-alkyl-(C=O)-NH-, C_6- to C_{10}-aryl-(C=O)-NH-, C_1- to C_{20}-alkyl-O-(C=O), C_1- to C_{20}-alkyl-NH-(C=O)-, or C_6- to C_{10}-aryl-NH-(C=O)-.

X^4 denotes hydrogen, halogen, cyano, nitro. CF_3, CCl_3, -COO-C_1 to C_4-alkyl or $X^{4'}$-R^4,

$X^{1'}$, $X^{2'}$ $X^{3'}$ and $X^{4'}$ denote a direct bond, -O-, -(N-R^5)-, -C(R^6R^7)-, -(C=O)-, -(CO-O)-. -(CO-NR^5)-, -(SO_2)- or (SO_2-O)- and

R^4. R^5, R^6, R^7 and R^8 independently of one another denote hydrogen, C_1- to C_4-alkyl. or C_6- to C_{10}-aryl and

R^4 and R^5 in addition independently of one another denote C_1- to C_{20}-alkyl-(C=O)-. C_3- to C_{10}-cycloalkyl-(C=O)-, C_2- to C_{20}-alkenyl-(C=O)-, C_6- to C_{10}-aryl-(C=O)-, C_1- to C_{20}-alkyl-(SO_2)-, C_3- to C_{10}-cycloalkyl-(SO_2)-. C_2- to C_{20}-alkenyl-(SO_2)-, or C_6- to C_{10}-aryl-(SO_2)-.

8. Process according to one or more of the preceding claims. wherein the storage medium on which information is to be written has a light-active layer of a thickness between 0.05 and 1000 µm.

9. Process according to one or more of the preceding claims. wherein the storage medium that is used has an optical density at the wavelength of the writing laser of the light-active layer of between 0.3 and 20.

10. Process according to one or more of the preceding claims. wherein in the storage medium that is used a depression is produced as a change in the surface topography of the light-active layer. said depression preferably having a depth of at least 10 nm.

11. Process according to one or more of the preceding claims. characterised in that a depression is produced in the storage medium having a width in one direction. measured on the original surface. of at least 10 µm.

12. Process according to one or more of the preceding claims, characterised in that the change in the surface topography of the storage medium is produced by laser light, preferably having wavelengths between 380 nm and 820 nm.

13. Process according to one or more of the preceding claims. characterised in that the light has an intensity of between 150 μW and 100 mW and is focused on spots having a dimension (full half-value width) in a range between 10 nm and 8 μm.

14. Process according to one or more of the preceding claims. characterised in that information can be written on storage media whose carrier layer comprises a polymer. preferably a thermoplastic polymer. particularly preferably polycarbonate.

15. Process according to one or more of the preceding claims. characterised in that a signal deviation is written in the storage medium having at least a carrier/noise ratio of 20 dB.

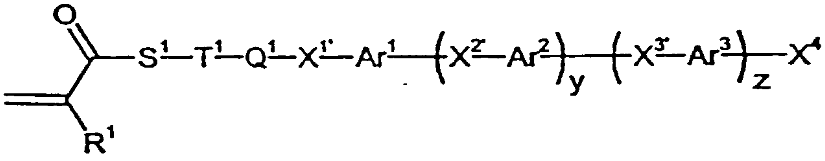
16. Process according to one or more of the preceding claims, wherein information can be written on storage media that contain, between the dye-containing layer and the further layer, an additional, light-reflecting layer, preferably from the group of metals comprising aluminium, silver, gold, particularly preferably from the group comprising aluminium and silver. and most particularly preferably aluminium.

17. Process according to one or more of the preceding claims. wherein the storage medium on which information is to be written has no reflecting layer.

18. Process according to one or more of the preceding claims. characterised in that the optical writing process is performed with polarised light of variable intensity, produced by a LASER with an acousto-optical modulator or by

modulation of a LASER diode, and the polarisation state of the reflected light is detected in a polarisation optics system.

19. Monomers of the formula

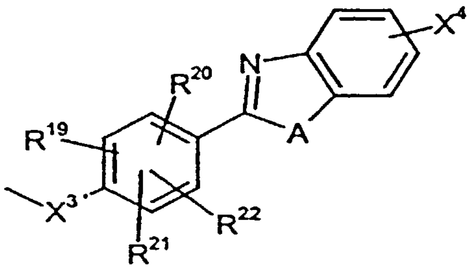

O
S¹
T¹
Q¹
X¹'
Ar¹
X²'
Ar²
y
X³'
Ar³
z
X⁴
R¹

(Ia)

wherein R^1 denotes hydrogen or methyl and

the other radicals have the meanings defined in claims 6 and 7, and

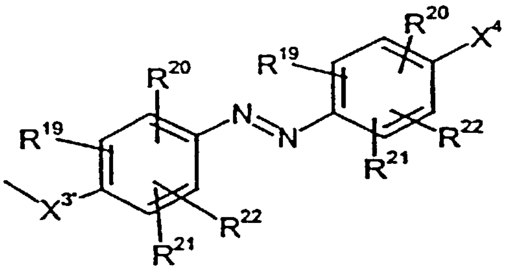
$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula


X⁴
N
R²⁰
A
R¹⁹
X³'
R²²
R²¹

$X^{3'}$ denotes –N=N- or –CO-NH-.

20. Monomers of the formula (Ia) according to claim 19, wherein

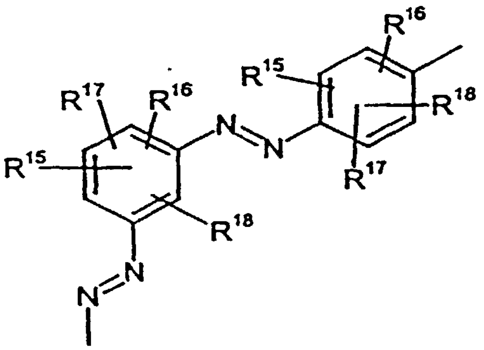
$-(X^{3'}-Ar^3)_z-X^4$ denotes a radical of the formula


R²⁰
X⁴
R²⁰
R¹⁹
N
R¹⁹
N
R²²
R²¹
X³'
R²²
R²¹

$X^{3'}$ denotes -O-, -(SO_2)-, -(C=O)-, -(N-R^5)-, -(CO-NR^5)- or -C(R^6R^7)-.

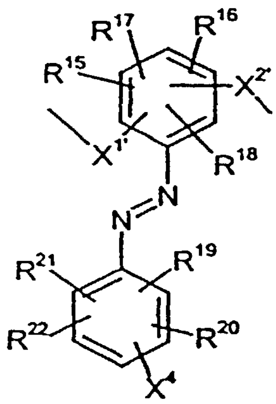
21. Monomers of the formula (Ia) according to claim 19, wherein

-($X^{2'}$-Ar^2)$_y$- denotes a bivalent radical of the formula


R16
R15
R18
R17
R17
R16
R15
R18
N
N
N
N

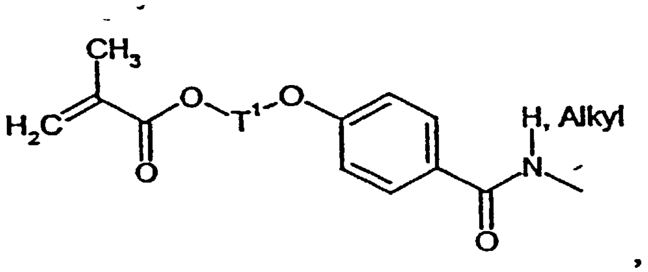
22. Monomers of the formula (Ia) according to claim 19, wherein

-($X^{1'}$-Ar^1)-$X^{2'}$denotes a bivalent radical of the formula


R17
R16
R15
X2'
X1'
R18
N
N
R21
R19
R22
R20
X4

wherein $X^{1'}$ and $X^{2'}$ are in the m- or p-position relative to one another and $X^{1'}$ and the azo group are in the o- or p-position relative to one another.

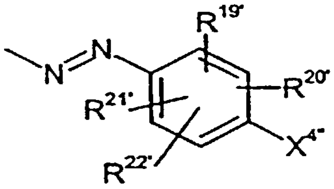
23. Monomers of the formula



$X^{2'}$ denotes –N=N- or –CO-NH-,

X^4 denotes hydrogen, C_1- to C_4- alkoxy, Di-C_1- to C_4-alkylamino, C_1-, to C_4- alkanoylamino, benzoylamino, cyano or nitro, wherein X^4 is particularly preferably in the p-position to the azo group,

R^{15} to R^{22} independently of one another denote hydrogen, methyl, methoxy or cyano, wherein one of the radicals R^{19} to R^{22} may denote a radical of the formula



which is particularly preferably in the m- or p-position relative to the azo group,

in which

$X^{4''}$ denotes hydrogen, C_1- to C_4-alkoxy, Di-C_1- to C_4-alkylamino, C_1- to C_4-alkanoylamino, benzoylamino, cyano or nitro and

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$R^{19'}$ to $R^{22'}$ independently of one another denote hydrogen, methyl, methoxy or cyano.

24. Polymers produced from monomers according to one or more of the preceding claims.

25. Use of the monomers according to claims 19 to 24 for producing optical storage media.

26. Storage media that can be obtained according to one or more of the preceding claims.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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Veröffentlicht:
— *Mit internationalem Recherchenbericht.*

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

WO 01/26105 A1

(54) Title: METHOD FOR DIGITALLY AND OPTICALLY STORING DATA

(54) Bezeichnung: VERFAHREN ZUR DIGITALEN OPTISCHEN DATENSPEICHERUNG

(57) Abstract: The present invention relates to a method for optically writing digital information into a flat, extended storage medium, whereby said information can also be optically read out afterwards.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren zum optischen Einschreiben danach auch wieder optisch

OIPE JC182
MAY 13 2002
PATENT & TRADEMARK OFFICE

COMBINED DECLARATION AND POWER OF ATTORNEY	ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought
on the invention entitled

METHOD FOR DIGITALLY AND OPTICALLY STORING DATA

the specification of which is attached hereto,

or was filed on **September 19, 2000**

as a PCT Application Serial No. **PCT/EP00/09269**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 47 579.2	**Germany**	**October 1, 1999**
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occured between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

[illegible]

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CITIZENSHIP:
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POST OFFICE ADDRESS: